

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/GB05/000802

International filing date: 04 March 2005 (04.03.2005)

Document type: Certified copy of priority document

Document details: Country/Office: GB
Number: 0422620.5
Filing date: 12 October 2004 (12.10.2004)

Date of receipt at the International Bureau: 02 May 2005 (02.05.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

GB05/802



INVESTOR IN PEOPLE



The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

Dated 11 April 2005



Patents Form 1/77

Patents Act 1977
(Rule 16)



13OCT04 E932906-1 D00192-
P01/7700 0.00-0422620.5 CHEQ
UE

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)



The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

1. Your reference

N.93051 CMK

2. Patent application number

(The Patent Office will fill this part in)

0422620.5

3. Full name, address and postcode of the or of each applicant (underline all surnames)

ISIS INNOVATION LIMITED
Ewert House, Ewert Place
Summertown
Oxford OX2 7SG

Patents ADP number (if you know it)

3998564003

United Kingdom

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

MODIFIED CARBON

5. Name of your agent (if you have one)

J. A. KEMP & CO.

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

14 South Square
Gray's Inn
London
WC1R 5JJ

Patents ADP number (if you know it)

26001

6. Priority: Complete this section if you are declaring priority from one or more earlier patent applications, filed in the last 12 months.

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. Divisionals, etc: Complete this section only if this application is a divisional application or resulted from an entitlement dispute (see note f)

Number of earlier UK application

Date of filing
(day / month / year)

8. Is a Patents Form 7/77 (Statement of inventorship and of right to grant of a patent) required in support of this request?

Yes

Answer YES if:

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body.

Otherwise answer NO (See note d)

Patents Form 1/77

9. Accompanying documents: A patent application must include a description of the invention. Not counting duplicates, please enter the number of pages of each item accompanying this form:

Continuation sheets of this form

Description

33 32

Claim(s)

6

Abstract

1

Drawing(s)

12 + 12

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for a preliminary examination and search (Patents Form 9/77)

1

Request for a substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature(s)

J.A. Kemp & Co

Date 12 October 2004

J.A. KEMP & CO.

12. Name, daytime telephone number and e-mail address, if any, of person to contact in the United Kingdom

Sally Gorsuch - 020 7405 3292

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered YES in part 8, a Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- Part 7 should only be completed when a divisional application is being made under section 15(4), or when an application is being made under section 8(3), 12(6) or 37(4) following an entitlement dispute. By completing part 7 you are requesting that this application takes the same filing date as an earlier UK application. If you want the new application to have the same priority date(s) as the earlier UK application, you should also complete part 6 with the priority details.

MODIFIED CARBON

FIELD OF THE INVENTION

The present invention relates to carbon which is modified with compounds
5 rendering it suitable for use in electrodes and electrochemical sensors.

DESCRIPTION OF THE PRIOR ART

Carbon-based electrode materials have been in use for many decades. The main
forms of carbon in common use are glassy carbon, carbon fibres, carbon black,
10 graphite, carbon paste and carbon epoxy electrode. Carbon is an attractive electrode
material as it is relatively chemically inert yet it has a high surface activity and a wide
operational potential window (ca. -1.0 V to +1.0 V vs. the saturated calomel electrode
in aqueous solution).

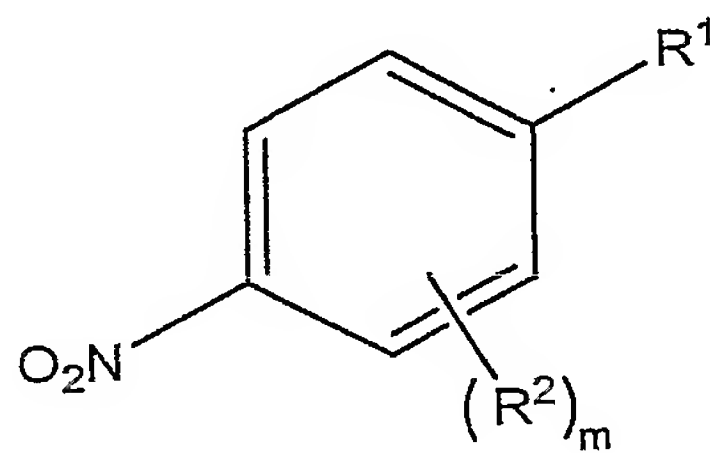
It is also known that carbon surfaces can be modified in order to produce
15 electrodes tailored to specific purposes. There are three main methods of modifying a
carbon surface: (i) by covalent attachment where the covalent bond formation is
activated either electrochemically via the direct chemical oxidation/reduction of the
modifier, or by the chemical activation of the modifier used to bring about the
modification; (ii) by physical adsorption (physisorption) of the modifier onto the carbon
20 surface; or (iii) modification through the use of carbon paste electrode where the paste
binder is doped with the modifier during preparation.

It is also known to intercalate small molecules and ions into various forms of
graphite. The small molecules are fully intercalated between the graphite sheets, which
in turn increases the interlayer spacing of the graphite, allowing for larger molecules to
25 be intercalated.

In the field of electrochemistry there is a constant need to prepare new
electrochemical sensors having increased selectivity and/or sensitivity to substances
which are to be measured. Accordingly, there is an ongoing need to identify new
materials with which to prepare such electrochemical sensors.

SUMMARY OF THE INVENTION

According to a first embodiment, the invention provides a novel method of chemical modification via partial intercalation of compounds into carbon. In particular, there is provided a method of modifying carbon by the partial intercalation of a compound which is a nitrobenzene derivative of formula (I):



(I)

wherein

- R^1 represents a group of formula $-\text{Y}$ or $-\text{X}-\text{Y}$ wherein Y is selected from hydrogen, hydroxy, C_{1-4} alkyl and $-\text{NR}^3\text{R}^4$ wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy, and wherein X represents a group of formula $-(\text{CR}^5\text{R}^6)_n-$ wherein n is 0 or an integer from 1 to 4 and R^5 and R^6 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl, C_{1-4} alkoxy or R^5 and R^6 together form a group of formula $=\text{O}$ or $=\text{NR}^7$ wherein R^7 is selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy;
 - R^2 is selected from hydroxy, halogen, C_{1-4} alkyl, C_{2-4} alkenyl, C_{1-4} alkoxy, C_{2-4} alkenyloxy, amino, C_{1-4} alkylamino, $\text{di}(\text{C}_{1-4} \text{ alkyl})\text{amino}$; C_{1-4} alkylthio, C_{2-4} alkenylthio, nitro, cyano, $-\text{O}-\text{CO}-\text{R}'$, $-\text{CO}-\text{O}-\text{R}'$, $-\text{CO}-\text{NR}'\text{R}''$, $-\text{COR}'$, $-\text{S}(\text{O})\text{R}'$ and $-\text{S}(\text{O})_2\text{R}'$, wherein each R' and R'' is the same or different and represents hydrogen, C_{1-4} alkyl or C_{2-4} alkenyl; and
 - m is 0 or an integer from 1 to 4;
- or a salt thereof, which method comprises mixing powdered carbon with a compound as defined above for a time sufficient to allow the compound to partially intercalate within the carbon, and isolating the resulting modified carbon.

The invention also provides a composition comprising modified carbon produced by this method.

The invention also provides a composition comprising carbon and a compound as defined above, wherein the compound is partially intercalated within the carbon.

The invention further provides an electrode for use in an electrochemical sensor, said electrode comprising a composition of the invention above.

5 The invention also provides a method for preparing an electrode for use in electrochemical sensors, said method comprising providing a substrate and applying a composition of the invention as defined above to the surface of said substrate.

The invention also provides the use of a compound as defined above in the manufacture of a composition comprising carbon, wherein said compound is partially
10 intercalated within the carbon. Also provided is the use in an electrode of carbon having partially intercalated within it a compound as defined above.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 discloses a schematic diagram illustrating the proposed partial
15 intercalation of 4-NBA into localised edge-plane defect sites along the surface of a MWCNT.

Figure 2 discloses the general mechanism for the electrochemical reduction of an aryl nitro moiety illustrated here by nitrobenzene.

Figure 3a shows twenty consecutive cyclic voltammograms of 4-NBAcarbon in
20 pH 6.8 buffer.

Figure 3b shows overlaid cyclic voltammograms recorded before and after replacing the pH 6.8 solution with fresh solution.

Figure 3c shows overlaid cyclic voltammograms of 4-NBAcarbon recorded after formation of the reversible couple corresponding to system II at varying scan rates (25,
25 50, 100, 200, 300, 400, 500, 600, 700, 800, 900 mVs⁻¹) in pH 6.8 buffer.

Figure 3d shows the corresponding plot of peak current vs. scan rate.

Figure 4a shows the 1st cyclic voltammograms (overlaid) of 4-NBAcarbon recorded in solutions of varying pH (pH 1.0, pH 4.6, pH 6.8, pH 9.2 and pH 12.0).

Figure 4b shows the corresponding plot of peak potential vs. pH.

30 Figure 5a shows overlaid square wave voltammograms (reductive sweep) of 4-NBA derivatised MWCNTs recorded in solutions of varying pH (pH 1.0, pH 4.6, pH 6.8, pH 9.2 and pH 12.0).

Figure 5b shows the corresponding plot of peak potential vs. pH.

Figure 6 is a plot of system I peak area vs. time for 4-NBA carbon sampled at various times during derivatisation. Error bars show the standard deviation over 5 samples.

5 Figure 7 shows five consecutive cyclic voltammograms of 4-NBA carbon in acetonitrile containing 0.1 M LiClO₄.

Figure 8 depicts a schematic model of 4-NBA partially intercalated into graphite showing that solvated Li⁺ cation may come into close contact with the 4-NBA molecule whereas the solvated NH₄⁺ cation may not.

10 Figure 9 shows a schematic model of the structure of graphite showing the approximate dimensions of a 4-NBA molecule and the graphite interlayer spacing for comparison.

Figure 10a shows a scanning electron microscopy image of MWCNTs modified with 4-NBA.

15 Figure 10b shows a scanning electron microscopy image of unmodified "native" MWCNTs.

Figure 11a shows a high resolution transmission electron microscopy image of a "bamboo-like" region of a MWCNT.

20 Figure 11b shows a high resolution transmission electron microscopy image of a "hollow tube" region of a MWCNT.

Figure 12 shows X-ray powder diffractograms comparing unmodified "native" MWCNTs with 4-NBA modified MWCNTs.

DETAILED DESCRIPTION OF THE INVENTION

25 The individual components and aspects of the invention will now be described in more detail.

As used herein, a C₁₋₄ alkyl group or moiety is a linear or branched alkyl group or moiety containing from 1 to 4 carbon atoms. Examples of C₁₋₄ alkyl groups and moieties include methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl and *t*-butyl. For the
30 avoidance of doubt, where two alkyl moieties are present in a group, the alkyl moieties may be the same or different.

As used herein, a C₂₋₄ alkenyl group or moiety is a linear or branched alkenyl group or moiety containing from 2 to 4 carbon atoms. For the avoidance of doubt, where two alkenyl moieties are present in a group, the alkenyl moieties may be the same or different.

5 As used herein, a halogen is typically chlorine, fluorine, bromine or iodine. It is preferably chlorine, fluorine or bromine.

As used herein the term amino represents a group of formula -NH₂. The term C₁₋₄ alkylamino represents a group of formula -NHR' wherein R' is a C₁₋₄ alkyl group, preferably a C₁₋₄ alkyl group, as defined previously. The term di(C₁₋₄ alkyl)amino
10 represents a group of formula -NR'R'' wherein R' and R'' are the same or different and represent C₁₋₄ alkyl groups as defined previously. As used herein the term amido represents a group of formula -C(O)NH₂.

As used herein, an alkoxy group is typically a said alkyl group attached to an oxygen atom. Similarly, alkenyloxy groups are typically a said alkenyl group attached
15 to an oxygen atom.

An alkylthio group is typically a said alkyl group attached to a thio group. Similarly, alkenylthio groups are typically a said alkenyl group attached to a thio group.

The alkyl and alkenyl groups or moieties in the compounds used in the invention are unsubstituted or substituted by one, two or three substituents which are
20 the same or different and are selected from hydroxy, halogen and unsubstituted C₁₋₂ alkoxy substituents.

As used herein, the term "partially intercalated" means that the compound defined above is partially located between sheets of carbon, rather than being located entirely between such sheets. The compound is localised within edge-plane defect sites
25 along the surface of the carbon, which can cause a slight increase in the interlayer spacing of the carbon. It has been found that the new materials having compounds defined above partially intercalated within can be manufactured by simple processes where the compounds spontaneously partially intercalate without the need for long reaction times or coupling agents.

30 This partial intercalation contrasts with known materials having intercalating compounds which are fully intercalated. When full intercalation occurs, the intercalating compounds are located entirely between adjacent sheets of graphite and

have the effect of pushing these sheets wide apart. This significantly increases the interlayer spacing of the carbon, which in turn allows subsequent intercalation of other, larger species. Production of carbon having fully intercalated compounds requires more experimentally and synthetically complicated processes than the new methods of the present invention.

Various methods can be used to determine whether a compound defined above has been partially intercalated within the carbon, as shown by the Examples which follow. A particularly useful technique is X-ray diffraction, which can distinguish between partially intercalated compounds and fully intercalated compounds. If the compound is fully intercalated in the carbon, then when the modified carbon is subjected to X-ray diffraction a peak will be observed corresponding to a considerably larger interlayer spacing than the native carbon which has not been modified. However, if the compound is partially intercalated, a broader peak will be observed, with the average interlayer spacing being the same as or slightly larger than the usual interlayer spacing for the carbon used. In particular, when such compounds are partially intercalated into multi-walled carbon nanotubes a significantly broader peak is observed at a slightly increased interlayer spacing.

Carbon

One form of carbon which is particularly suitable for use in the invention is graphite. The graphite is preferably in the form of powdered graphite. A suitable particle diameter is from 0.1 to 100 μm , more preferably from 1 to 50 μm and more preferably from 2 to 20 μm .

Another form of carbon which is particularly suitable for use in the invention is multi-walled carbon nanotubes. Carbon nanotubes (CNTs, also referred to herein as nanotubes) have been known for a number of years, having been discovered in 1991 (see S. Iijima, *Nature*, 1991, 56, 354). One field that has seen a large expansion in the study and use of nanotubes is electrochemistry. Carbon nanotubes are particularly useful in this field due to their noted mechanical strength, structure and good electrical conductivity. These properties have been used in electroanalytical applications ranging from catalytic detection and analysis of biological molecules such as dopamine.

cytochrome c and carbohydrates, to the sensing of analytes such as hydrogen peroxide, hydrazine and TNT.

Structurally, nanotubes approximate to "rolled up" sheets of graphite and as such are relatively hydrophobic in nature. There are two main configurations of these "rolled up" sheets: single-walled carbon nanotubes (SWCNTs) which are formed as a single, hollow, graphite tube, and multi-walled carbon nanotubes (MWCNTs) which consist of several concentric graphite tubes fitted one inside the other. In the present invention MWCNTs can be used.

Suitable nanotubes include those purchased from Nanolab Inc. (Brighton, MA, USA). The physical properties of the nanotubes can be optimised by the person skilled in the art, although exemplary nanotubes have a diameter of from 1 to 50 nm, preferably from 5 to 30 nm, and a length of from 1 to 50 μ m, preferably from 5 to 30 μ m. Preferably the carbon nanotubes have a relatively high purity, preferably from 80 to 100%, more preferably from 90 to 100%, most preferably from 95 to 100%.

Partially Intercalating Compounds

The compounds used in the invention are described earlier. The compounds may be in the form of nitrobenzene derivatives of formula (I) or salts thereof. The alkyl and alkenyl groups or moieties in the compounds are unsubstituted or substituted by one, two or three substituents which are the same or different and are selected from hydroxy, halogen and unsubstituted C_{1-2} alkoxy substituents.

Preferably the R^2 substituent is selected from hydroxy, halogen, C_{1-4} alkyl, C_{2-4} alkenyl, C_{1-4} alkoxy, C_{2-4} alkenyloxy, amino, C_{1-4} alkylamino, di(C_{1-4} alkyl)amino, C_{1-4} alkylthio, C_{2-4} alkenylthio, nitro or cyano. More preferably R^2 is selected from hydroxy, halogen, C_{1-4} alkyl, C_{1-4} alkoxy, amino, C_{1-4} alkylamino and di (C_{1-4} alkyl)amino. More preferably R^2 is selected from hydroxy, halogen, C_{1-4} alkyl and C_{1-4} alkoxy.

The number of R^2 substituents can vary between zero and four. Preferably the number of R^2 substituents, represented by m, is zero, one or two. More preferably m is zero or one, most preferably zero.

X represents a group of formula $-(CR^5R^6)_n-$ where n is zero or an integer from one to four. Preferred R^5 and R^6 groups include hydrogen, hydroxy, C_{1-2} alkyl and C_{1-2} alkoxy, with hydrogen being preferred.

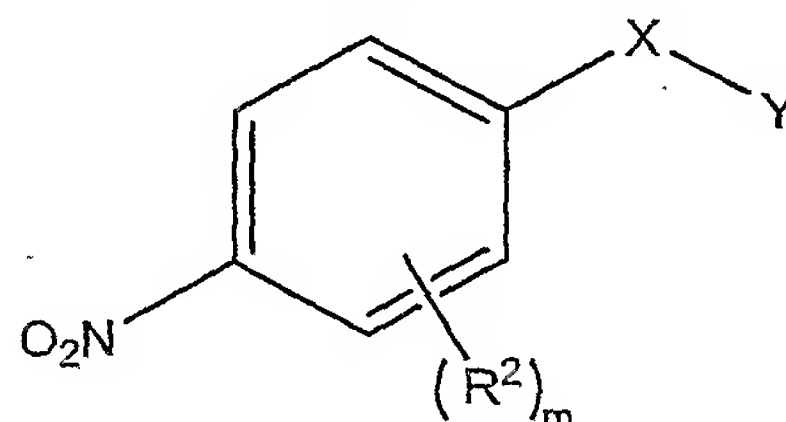
5 The alkyl groups or moieties in the X group are unsubstituted or substituted by one, two or three substituents which are the same or different and are selected from hydroxy, halogen and unsubstituted C_{1-2} alkoxy substituents. Preferably the R^5 and R^6 groups in the X group are unsubstituted.

Preferably n is zero, one or two. Most preferably n is one.

10 The group Y is selected from hydrogen, hydroxy, C_{1-4} alkyl and $-NR^3R^4$ wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy. The alkyl groups or moieties in Y are unsubstituted or substituted by one, two or three substituents which are the same or different and are selected from hydroxy, halogen and unsubstituted C_{1-2} alkoxy substituents. Preferably the alkyl groups or moieties in Y are unsubstituted.

15 Preferred Y groups are $-NR^3R^4$. When Y is $-NR^3R^4$, R^3 and R^4 are the same or different and are preferably hydrogen, hydroxy, C_{1-2} alkyl or C_{1-2} alkoxy. More preferably R^3 and R^4 are selected from hydrogen and C_{1-2} alkyl. Most preferably both R^3 and R^4 are both hydrogen.

Preferred compounds are nitrobenzene derivatives of formula (II):



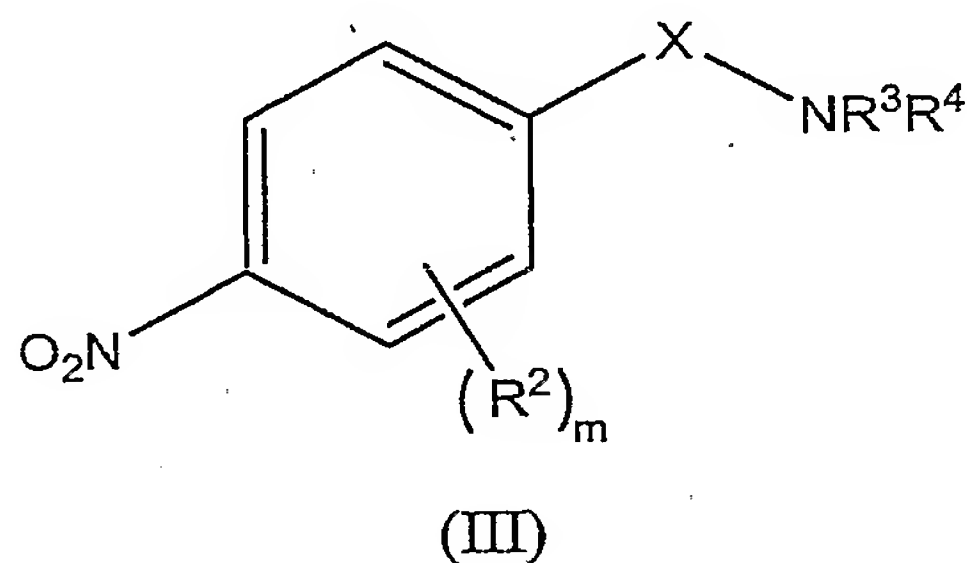
(II)

wherein:

- R^2 is selected from hydroxy, halogen, C_{1-4} alkyl and C_{1-4} alkoxy;
- m is 0, 1 or 2;
- 25 - X represents a group of formula $-(CR^5R^6)_n-$ wherein n is 0, 1 or 2 and R^5 and R^6 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl, C_{1-4} alkoxy; and

- Y is selected from hydrogen, hydroxy, C₁₋₄ alkyl and -NR³R⁴ wherein R³ and R⁴ are the same or different and are selected from hydrogen, hydroxy, C₁₋₄ alkyl and C₁₋₄ alkoxy, or salts thereof.

5 Further preferred compounds are nitrobenzene derivatives of formula (III):

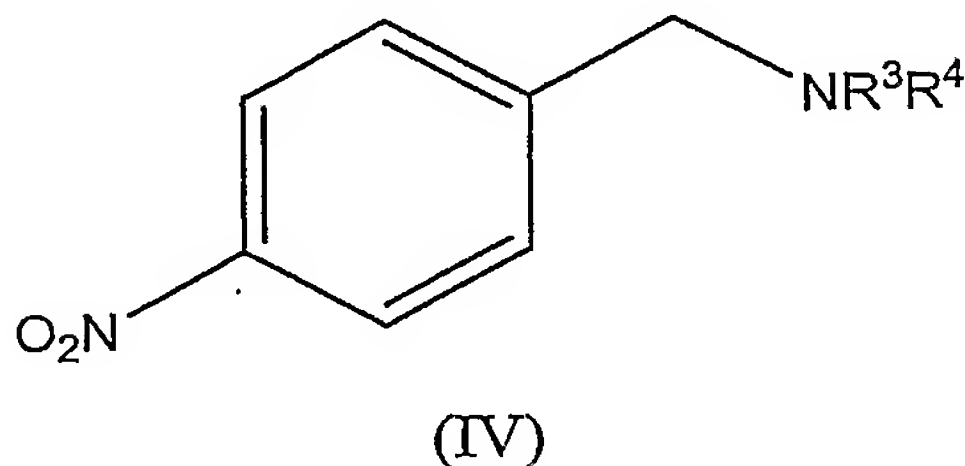


wherein:

- R² is selected from hydroxy, halogen, C₁₋₄ alkyl and C₁₋₄ alkoxy;
- 10 - m is 0, 1 or 2;
- X represents a group of formula -(CR⁵R⁶)_n- wherein n is 0, 1 or 2 and R⁵ and R⁶ are the same or different and are selected from hydrogen, hydroxy, C₁₋₄ alkyl and C₁₋₄ alkoxy; and
- R³ and R⁴ are the same or different and are selected from hydrogen, hydroxy, C₁₋₄ alkyl and C₁₋₄ alkoxy,
- 15 or salts thereof.

Preferably m is zero or one, more preferably m is zero. Preferably n is one, with R⁵ and R⁶ being the same or different and selected from hydrogen, hydroxy, C₁₋₄ alkyl and C₁₋₄ alkoxy. More preferably R⁵ and R⁶ are the same or different and are selected from hydrogen and C₁₋₄ alkyl. Most preferably both R⁵ and R⁶ are hydrogen.

20 More preferred compounds used in the invention are nitrobenzene derivatives of formula (IV):



wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy, or salts thereof. More preferably R^3 and R^4 are the same or different and are selected from hydrogen and C_{1-4} alkyl.

The compounds used to make the compositions of the invention include salts of the nitrobenzene derivatives of formulae (I) to (IV). These salts can be any suitable salt which allows does not interfere with the electrochemical mechanisms which allow the compounds to be useful in electrodes and electrochemical sensors. In particular, there can be mentioned inorganic and organic acid addition salts. Suitable inorganic acids which can be used include hydrochloric, sulphuric, phosphoric, diphosphoric, hydrobromic or nitric acid. Suitable organic acids which can be used include citric, fumaric, maleic, malic, ascorbic, succinic, tartaric, benzoic, acetic, methanesulphonic, ethanesulphonic, benzenesulphonic or p-toluenesulphonic acid. The salts may also be formed with bases, for examples with alkali metal (e.g. sodium or potassium) and alkaline earth metal (e.g. calcium or magnesium) hydroxides and organic bases such as alkyl amines, aralkyl amines or heterocyclic amines.

Without wishing to be bound by theory, it is believed that the compounds used in the invention partially intercalate into localised edge-plane defect sites along the carbon surface of both graphite and carbon nanotubes. The redox characteristics of carbon modified with these compounds show that the modified materials can be used in electrochemical sensors, for example for the measurement of pH.

In particular, the compounds used in the invention and the modified carbon of the invention are useful in the manufacture of electrodes for measuring pH. In this regard, the voltammetry of such compounds has been studied. The voltammetry of such compounds sensitive to pH, when immobilised as molecular solids onto the surface of an electrode, has been found to exhibit Nernstian behaviour which can be described according to the following Nernst equation (1):

$$E_p = E_f^0 - \frac{2.3RTm}{nF} pH \quad (1)$$

where E_p / V is the peak potential, E_f^0 / V is the formal potential of the redox couple, R / $J K^{-1}$ is the universal gas constant, T / K is the temperature and m and n are the number of protons and electrons involved in the redox process respectively.

Accordingly, by studying the voltammetric response of these compounds, for example using cyclic voltammetry or square-wave voltammetry, a linear response of peak potential to pH would be expected.

5 Other redox active materials

As well as the compounds defined above, other redox active materials can be included in the materials of the invention. These additional redox active materials may be any organic material capable of undergoing electron loss and gain. Preferably the additional redox active material is a solid phase material. When immobilised onto a
10 substrate, e.g. glassy carbon or a basal plane pyrolytic graphite (bppg) electrode, it undergoes concomitant proton and electron loss/gain on oxidation/reduction.

The additional redox active material may be sensitive or insensitive to the species which is to be detected or measured. In either case, by measuring the potential difference between the current peaks for the compounds defined earlier and for the
15 additional redox active material, the concentration of the species to be measured can be determined.

It is preferred that the electrodes of the invention be useful in the manufacture of pH meters, and accordingly in one embodiment the additional redox active material is sensitive to the concentration of protons. Preferably the peak potential of the additional
20 redox active material depends on the local proton concentration. As discussed above in relation to the compounds used in the invention (i.e. the nitrobenzene derivatives or salts thereof) the voltammetry of redox active materials which are sensitive to pH has been found to show Nernstian behaviour. Accordingly, by studying the voltammetric response of these compounds, for example using cyclic voltammetry or square-wave
25 voltammetry, a linear response of peak potential to pH would be expected.

More than one additional redox active material may be used in the invention. Suitable additional redox active materials include quinones and anthracenes, for example 9,10-anthracene, 9-nitroanthracene, phenanthraquinone (PAQ) and 1,2-naphthaquinone (NQ). Other materials that can be used include azobenzene,
30 diphenylamine, methylene blue, 3-nitrofluoranthene, 6-nitrochrysene and thionin.

When present, the additional redox active material can be combined with the modified carbon by any suitable process. For examples, in one embodiment of the

invention the additional redox active material can be combined with the modified carbon by chemisorption of aryldiazonium salts using hypophosphorous acid as the chemical reducing agent. In another embodiment of the invention phenanthraquinone (PAQ) can be physisorbed onto graphite.

5 In another embodiment of the invention the additional redox active material can be combined with the modified carbon described previously by way of agglomeration. Such agglomerates comprises (i) carbon nanotubes having a compound as defined above which is a nitrobenzene derivative of formula (I) or a salt thereof partially intercalated within, and (ii) a binder, wherein the binder is the additional redox active
10 material. The nanotubes, compound and additional redox active material may be as described above.

In this embodiment, the agglomerate is made by dispersing the nanotubes in a binder. The preferred method comprises combining MWCNTs having a compound of as defined above partially intercalated within (hereafter "the modified MWCNTs") and
15 binder material in a solvent, and then precipitating the agglomerate out of the solution. In particular, the method may comprise:

- (1) combining the modified MWCNTs and the binder in a solvent;
- (2) adding an excess of aqueous solution in order to cause precipitation of the agglomerate out of the solvent; and
20 (3) recovering the agglomerate.

Preferably the solvent is a hydrophobic solvent, comprising small organic molecules. The solvent should be chosen such that the redox active compound and the carbon nanotubes are both soluble within it. Suitable solvents include all common organic solvents such as acetone, acetonitrile and dimethyl formamide.

25 In this embodiment, it is preferred that the additional redox active materials are hydrophobic, having a low solubility in water. This allows them, when an agglomerate is being manufactured, to mix with the carbon nanotubes in solution and results in the agglomerate precipitating out of solution when an excess of aqueous solution is added.

The agglomerate preferably comprises the modified MWCNTs and additional
30 redox active materials only, with no other materials present. However, the agglomerate may contain some impurities such as residual solvent, left as a result of a process by which the agglomerate is be produced. Preferably these impurities comprise less than 1

wt% of the agglomerate, more preferably less than 0.5 wt%. The precise level of impurities which is acceptable in the agglomerate will depend upon how the impurities affect the voltammetry of the agglomerate.

5 The size of the agglomerates depends upon the nature and proportions of the components used in their preparation and the conditions of the process by which they are prepared. However, exemplary agglomerates may be approximately 10 μ m in diameter and consist of bundles of nanotubes running into and throughout an amorphous molecular solid which binds the agglomerate together.

10 The agglomerate is preferably applied to the substrate of the electrode by way of abrasive immobilisation.

The Substrate

15 The substrate onto which is applied the modified carbon may be any substrate conventionally used in the manufacture of electrodes. For example, the substrate may be a basal plane pyrolytic graphite (bppg) electrode or glassy carbon, metal electrodes such as gold or platinum, or optically transparent electrodes such as those comprising ITO. The substrate preferably has good electrical contact with the carbon nanotubes, and also has a surface such that good coverage with the carbon nanotubes and redox active material can be achieved.

20

The Sensor

25 The structure of sensors according to the invention will depend upon the final application of the sensor, and depends upon the substance which the sensor is to measure and the environment in which measurement will take place. Known sensor structures may be employed in conjunction with the agglomerates and electrodes described herein.

30 Exemplary sensors may have a two or three terminal arrangement. Thus, they may comprise a working electrode of the invention and a combined counter and reference electrode, or a working electrode, counter electrode and separate reference electrode. The reference electrode and counter electrode can be any conventional electrodes known in the art.

The materials used in the sensor depend upon which species the sensor is intended to measure and the environment in which the sensor is to be used. In order to modify the sensor to be sensitive to a different species it is simply required for the skilled person to substitute the partially intercalating compound defined above (i.e. the
5 nitrobenzene derivative or salt thereof) or additional redox active material with a different partially intercalating compound or additional redox active material sensitive to the species which is to be measured.

The modified carbon materials of the invention are particularly suited for use in "single-shot" pH sensors for use in "dirty" environments, such as effluent or sewage,
10 where recovery of the sensor is likely to be undesirable.

Method for preparing the modified carbon of the invention

Carbon is modified according to the method of the invention by mixing the carbon in a solvent with a partially intercalating compound defined above. Suitable
15 solvents include common aprotic organic solvents. For example, there can be mentioned dimethyl formamide (DMF), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), acetone, acetonitrile, ethyl acetate, chloroform, methylene chloride. The solvent may be degassed or may contain dissolved gases, e.g. dissolved oxygen.

The carbon, solvent and compound are mixed for a time sufficient to allow
20 partial intercalation of the compound into the carbon. A suitable time is 1 to 5 hours, although longer or shorter time periods can also be used. After this time the modified carbon is filtered, washed with solvent in order to remove any physisorbed species, and dried. One particular advantage of this method is that it can proceed without the need for a coupling agent.

25 The relative amount of the compound and carbon can be chosen by the skilled person according to the end use of the modified carbon.

Surprisingly the compounds used in the invention spontaneously partially intercalate into the carbon. The resulting materials are robust, for example when used in electrochemical sensors, producing stable responses at elevated temperatures.
30 Furthermore, the compounds partially intercalate at a high level, i.e. a large amount of the compounds can be partially intercalated. This results in large current response and high sensitivity.

The following Examples illustrate the invention.

EXAMPLES

5 All reagents were obtained from Aldrich (Gillingham, UK) with the exception of potassium chloride (Riedel de Haën, Seelze, Germany) tetrabutylammonium perchlorate (TBAP), lithium perchlorate (Fluka Chemicals, Gillingham, UK) acetonitrile (synthesis grade, 99.99% anhydrous, Fischer Scientific, Loughborough, UK) diethyl ether (British Drug House Chemicals, Poole, UK) and were of the highest grade available and used without further purification.

10 4-nitrobenzylamine (4-NBA) was obtained as the hydrochloride salt. In order to liberate the free amine the following procedure was used: 4-nitrobenzylamine hydrochloride salt (2.0 g, 0.011 mmol) was dissolved in water (40 cm³) and sodium hydroxide (20 cm³ of a 1 M aqueous solution) was added. The solution was stirred for 2 hours, after which time the solution was washed with diethyl ether (2 x 50 cm³). The
15 combined organic layers were washed with brine (50 cm³), dried over MgSO₄, filtered and concentrated in vacuo to afford 4-nitrobenzylamine (1.2 g, 78% yield) as a red crystalline solid which was used without further purification. The corresponding nuclear magnetic resonance spectrum was recorded and compared with library spectra in order to confirm that the pure compound had been re-crystallised. The crystals of 4-
20 NBA were stored in an air-tight container at 4 °C prior to use.

Aqueous solutions were prepared using deionised water from an Elgastat (Elga, UK) UHQ grade water system with a resistivity of not less than 18.2 MΩ cm. Non-aqueous solutions were prepared using acetonitrile (supplied as 99.99% anhydrous), which was dried over 5 Å molecular sieves for 24 hours prior to use to remove any
25 trace water content. Cyclic voltammetric measurements were made after degassing the solution with pure N₂ gas (BOC gases, Guildford, Surrey, UK) for 30 minutes and carried out at 20 ± 2 °C.

Synthetic graphite powder (2-20 µm diameter) was purchased from Aldrich. Multiwalled carbon nanotubes (purity >95 %, diameter 10-40 nm, length 5-20 µm)
30 were purchased from NanoLab Inc. (Brighton, MA, USA) and were used without further purification.

Solutions of known pH in the range pH 1.0 to pH 12.0 were made up in deionised water as follows: pH 1.0, 0.10 M HCl; pH 4.6, 0.10 M acetic acid + 0.10 M sodium acetate; pH 6.8, 0.025 M Na_2HPO_4 + 0.025 M KH_2PO_4 ; pH 9.2, 0.05 M disodium tetraborate; pH 12, 0.01 M sodium hydroxide. These solutions contained in addition 0.10 M KCl as supporting electrolyte. pH measurements were performed using a Jenway 3030 pH meter.

Electrochemical measurements were recorded using a μ Autolab computer controlled potentiostat (Ecochemie, Utrecht, Netherlands) with a standard three-electrode configuration. All experiments were carried out in a glass cell of volume 25 cm^3 . A basal plane pyrolytic graphite electrode (bppg, 0.20 cm^2 , Le Carbone Ltd, Sussex, UK) acted as the working electrode (see below). A platinum coil (99.99% Goodfellow, Cambridge, UK) acted as the counter electrode. The cell assembly was completed either by using a saturated calomel electrode (SCE, Radiometer, Copenhagen, Denmark) as a reference electrode in aqueous solution, or by using a silver wire (99.99% Goodfellow, Cambridge, UK) as a quasi-reference electrode in non-aqueous solution.

Unless stated otherwise cyclic voltammograms were recorded using the following parameters: step potential 2 mV, scan rate 100 mVs^{-1} . Square-wave voltammetric parameters were as follows: frequency 12.5 Hz, step potential 2 mV and amplitude 25 mV.

Scanning electron microscopy (SEM) images were recorded using a Jeol 6500F instrument. High resolution transmission electron microscopy (HRTEM) images were recorded using a Jeol 2010F instrument.

X-ray powder diffraction experiments were carried out using a Panalytical Xpert Pro instrument utilising X-ray radiation from the copper $\text{K}\alpha_1$ band ($\lambda = 1.54 \text{ \AA}$).

Example 1:

Protocol for the derivatisation of graphite powder and multiwalled carbon nanotubes (MWCNTs) with 4-NBA and their abrasive immobilisation onto the surface of a bppg electrode:

Derivatisation of graphite powder (0.5 g) or MWCNTs (50 mg) with 4-nitrobenzylamine (4-NBA) was achieved by stirring either the graphite powder sample

or the MWCNT sample in a solution of 4-NBA in acetonitrile (10 mM, 25 cm³) for 120 minutes at room temperature unless otherwise stated. Next, the sample was filtered under suction, washed with acetonitrile (5 x 50 cm³) to remove any physisorbed species and air dried for 12 hours. After which, the sample was stored in an air-tight container prior to use.

The derivatised carbon powders or MWCNTs were then abrasively immobilised onto the surface of a clean bppg electrode prior to any electrochemical experiment. This was achieved by initially polishing the bppg electrode on glass-polishing paper (H00/240), after which it was polished on silicon carbide paper (P1000C) for smoothness. The 4-NBAcarbon (i.e. graphite having 4-NBA partially intercalated within) or 4-NBAMWCNTs (i.e. MWCNTs having 4-NBA partially intercalated within) were then abrasively immobilised onto the bppg electrode by gently rubbing the electrode surface on a fine filter paper (Whatman) containing the 4-NBAcarbon or 4-NBAMWCNTs.

Example 2:

Voltammetric Characterisation of graphite powder and MWCNTs derivatised with 4-nitrobenzylamine:

Cyclic voltammetry (CV) was used in order to confirm that 4-NBA molecules are attached onto the graphite powder (4-NBAcarbon), or onto the MWCNTs (4-NBAMWCNTs), which themselves are abrasively immobilised onto a bppg electrode. A standard protocol (given below) was employed over the entire pH range (pH 1.0 to pH 12.0).

First, twenty repeat scans were recorded to ensure that the redox species in question (4-NBA) is stable when in contact with an aqueous solution and does not desorb from the electrode surface. Figure 3a shows twenty repetitive cycles of 4-NBAcarbon on bppg in pH 6.8 buffer. As can be seen from figure 3a, it is necessary to sweep the potential in a reducing direction to ca. -1.0 V vs. SCE, past an irreversible redox process at ca. -0.6 V vs. SCE (labelled as "system I" in figure 3a and figure 2), in order to generate an electrochemically almost-reversible couple at ca -0.1 V vs. SCE (labelled as "system II" in figure 3a and figure 2). The exact potentials of the redox processes discussed above will depend on the pH of the solution. At every pH studied

in the range pH 1.0 to pH 12.0 a wave shape that was almost symmetrical and had a slight peak to peak separation that increased with increasing scan rate was observed. It was found that after twenty repetitive scans the peak currents (which were initially found to decrease slightly) remained stable and that the charges (peak areas) of both the oxidative and reductive peak processes were almost equal to each other (figure 3a).

The next step was to replace the electrolyte solution with fresh solution and record the voltammetric response. The corresponding cyclic voltammograms were found to overlay the last scan at every pH studied, thereby confirming that the electroactive species remains on the electrode and is not released to solution. Figure 3b shows the overlaid CVs after replacing pH 6.8 solution with fresh solution.

Finally, after formation of the reversible couple (system II), as described above, the scan rate was varied from 25 to 900 mVs⁻¹ (figure 3c) and a plot of peak current versus scan rate (figure 3d) was found to be almost linear, consistent with a surface bound species. However the peak separation of (ca. 100 mV at low scan rates) is considerably larger than the theoretical zero peak to peak separation for an ideal, immobilised, electrochemically reversible species. These discrepancies may possibly be due to some slight ohmic distortion at higher scan rates and/or electrode kinetic factors. In fact the wave shapes and the variation of peak potential with increasing scan rate suggest that an electrochemically quasi-reversible immobilised system exists over the entire pH range studied.

Example 3:

Voltammetric response of 4-NBAcarbon and 4-NBAMWCNTs from pH 1.0 to pH 12.0:

Having characterised these materials from pH 1.0 to pH 12.0 using cyclic voltammetry, this Example now demonstrates that these modified carbon materials can be used for the analytical sensing of pH. As shown in Figure 2, the electrochemical reduction of aromatic nitro compounds such as 4-NBA undergoes an initial irreversible step involving four-electrons and four-protons to form the corresponding arylhydroxylamine. Upon repetitive cycling the arylhydroxylamine can then undergo a chemically reversible, electrochemically quasi-reversible oxidation to the corresponding aryl nitroso compound, involving a further two-electrons and two-protons.

The peak potentials for these processes must therefore depend on the local proton concentration and hence must be sensitive to variations in pH. The variation in peak potential with pH can be described by the Nernst equation (1) discussed earlier. In this Example $n=m$ and is likely to be equal to two in the case of the reversible process (system II in figure 2).

Figure 4a shows the overlaid cyclic voltammograms (first scan) recorded in a range of solutions of differing pH (pH 1.0, 0.10 M HCl; pH 4.6, 0.10 M acetic acid + 0.10 M sodium acetate; pH 6.8, 0.025 M Na_2HPO_4 + 0.025 M KH_2PO_4 ; pH 9.2, 0.05 M disodium tetraborate; pH 12.0, 0.01 M sodium hydroxide) for 4-NBA carbon on bppg.

A plot of peak potential vs. pH for the peak corresponding to system I in figure 2 and both the oxidative and reductive peaks corresponding to system II in figure 2 is presented in figure 4b. The plots of peak potential vs. pH produced in each case a linear response with a corresponding R^2 value of not less than 0.9943. The gradient of such a plot for the oxidative and reductive peaks of system II yielded values of 60.4 mV / pH unit and 59.8 mV / pH unit respectively. This is close to the ideal theoretical gradient of 59.1 mV / pH unit at 298 K predicted by the Nernst equation.

A similar plot of peak potential vs. pH for the irreversible system I yielded a gradient of 42.5 mV / pH unit. This clearly deviates from the Nernstian behaviour predicted by the equation (1). This may be partly explained by the fact that the Nernst equation (1) is derived for systems exhibiting reversible kinetics,¹ whilst system I is clearly chemically and electrochemically irreversible. Furthermore similar results of a ca. 40 mV / pH unit shift were obtained by Wain et al. in their studies of microdroplets of 4-nitrophenol-nonyl-ether on a bppg electrode immersed in aqueous solutions of varying pH. They attributed this deviation from Nernstian behaviour to possible competition between H^+ and alkali metal cations such as K^+ and especially Li^+ . The fact that system I rapidly vanishes after the first couple of scans makes these modified carbon materials of the invention ideally suited for use as "single-shot" pH sensors for use in media, such as effluent and sewerage, where recovery of the sensor is unlikely to be desirable.

The reversible, Nernstian redox processes corresponding to the oxidation/reduction of the arylhydroxylamine/arylnitroso moieties of 4-NBA remain stable for many tens of scans. The variation of this redox couple with pH was

investigated further using the technique of square wave voltammetry. Square wave voltammetry has significant advantages over conventional cyclic voltammetry, as it provides a means of carrying out a single sweep, producing a well-defined voltammetric peak as the arylhydroxylamine/arylnitroso couple has nearly reversible kinetic behaviour. Figure 5a shows the corresponding overlaid reductive square wave voltammograms recorded at each pH studied for 4-NBAMWCNTs. It is worth noting that at pH 1.0 the oxidative wave is somewhat distorted due to the presence of an azoxy linkage affecting the redox chemistry. This causes some deviation from linearity in a plot of peak potential vs. pH at low pH values (figure 5b). Furthermore an extra peak is observed at pH 12.0 that was not observed in the cyclic voltammograms at this pH. The presence of this peak can be attributed to the formation of the radical anion of the nitro-group upon reduction which is relatively stable and electrochemically reversible at such alkaline pHs. Its presence is observed in square wave but not in cyclic voltammetry due to the high sensitivity of the technique. It is apparent from figure 5b that a plot of peak potential vs. pH taken from the square wave data produces a linear, Nernstian response (apart from the deviation at low pH), with gradients of 62.8 mV / pH unit and 59.2 mV / pH unit for the oxidative and reductive processes respectively and R^2 values greater than 0.9998. This again is in excellent agreement with theory (equation 1).

20 Example 4: Characterisation of 4-NBAcarbon and 4-NBAMWCNTs

The nature of the surface modification of the carbon used in the Examples above was then investigated to determine whether the compound of formula (I) (in this case 4-NBA) had indeed been intercalated and in particular to determine whether it had been partially intercalated. In terms of modification of carbon by a compound, there are three general possibilities: (i) physical adsorption (physisorption), (ii) chemical adsorption (chemisorption) and (iii) full or partial intercalation.

Example 4.1 Test for physical adsorption (physisorption) of 4-NBA onto graphite and MWCNTs

30 The inventors investigated how the length of time the reaction mixture was stirred during the derivatisation procedure affected the amount of 4-NBA absorbed by the carbon material. In order to do this an aliquot of the reaction mixture, which

contained graphite particles or MWCNTs suspended in a 10 mM solution of 4-NBA in acetonitrile, was removed, filtered, washed with dry acetonitrile and dried at 40 minute intervals until 160 minutes of stirring had elapsed. The samples were then abrasively immobilised onto a bppg electrode and cyclic voltammetry was carried out in pH 6.8 buffer. Five scans were recorded for each sample, and five samples were separately abrasively immobilised for each aliquot removed at a given time. From the five cyclic voltammograms recorded for each sample, the peak areas corresponding to the irreversible four-electron, four-proton reduction of the nitro-group moiety at -0.6 V vs. SCE in figure 3a, and the reversible two-electron, two-proton arylhydroxylamine/arylnitroso couple at -0.1 V vs. SCE in figure 3a were measured. These peaks are labelled as system I and system II respectively in figure 2.

The peak area is the amount of charge passed during a redox process and can therefore be directly related to the number of moles of 4-NBA on the carbon surface using Faraday's Laws. This was repeated for each of the five samples taken at each time interval. Because the exact amount of material immobilised onto the electrode surface cannot be accurately controlled using abrasive immobilisation, the data from each of the five cyclic voltammograms recorded for each of the five samples (twenty-five cyclic voltammograms in total for each time period investigated) was averaged and plotted against time. The standard deviation was calculated as an error bar for each point showing the dispersion of data over the five abrasive immobilisations carried out for each time interval.

Figure 6 shows a plot of peak area vs. time recorded for the irreversible reduction peak at -0.6 V vs. SCE of 4-NBA derivatised graphite. Also shown on this graph for comparison are the theoretical maximum charges passed for a monolayer of 4-NBA molecules covering the geometric area of the bppg electrode, and for a monolayer of 4-NBA coating the surface of the graphite particles (modelled as spheres) which themselves are close-packed as a monolayer on the geometric surface of the electrode. This model is a gross oversimplification as first the true surface area of a bppg electrode is always larger than its geometric area due to the surface not being perfectly smooth, and second the abrasive immobilisation of graphite particles onto the electrode surface is likely to produce multiple layers of particles which are not necessarily going to be close packed due to the uneven shape and size distributions of

the particles. However such a calculation is useful in that it provides us with an indication of the degree of modification by the 4-NBA molecules.

Figure 6 shows that at longer reaction times the amount of immobilised 4-NBA reaches a maximum value showing saturation. Analogous results were observed for both the oxidative and reductive peaks belonging to system II in figure 2, and in the case of MWCNT derivatisation. Whilst this experiment in itself does not provide evidence for intercalation it gives an interesting insight into the "filling-up" of the sites at which 4-NBA can modify the carbon surface. This effect would also be observed if physisorption led to only a monolayer formed on the surface. In fact it is important to note that the fact that the number of sites where 4-NBA can modify the MWCNTs or graphite powder is limited is consistent with any of the three hypothesis presented in this report, physical adsorption, chemical adsorption or intercalation of 4-NBA.

The derivatised carbon powders/MWCNTs are washed with a large quantity of dry acetonitrile during the derivatisation procedure, with the specific aim of removing any physisorbed material which is known to desorb when treated with non-aqueous solvents. It is therefore highly improbable that surface physisorption is the mechanism of modification in this case.

Further evidence against physisorption arises from the fact that we have carried out electrochemical experiments using cyclic voltammetry on 4-NBAcarbon and 4-NBAMWCNTs in acetonitrile solutions with 0.1 M TBAP and 0.1 M LiClO₄ as supporting electrolyte (see below). However, slow desorption kinetics of 4-NBA from the MWCNTs or graphite powder may explain the fact that voltammetry can be observed from 4-NBAcarbon and 4-NBAMWCNTs in acetonitrile. Therefore in order to verify that slow desorption kinetics were not responsible for our experimental observations described above, the following experiment was performed. In this experiment, 4-NBAcarbon was abrasively immobilised onto a bppg electrode. The electrode was then immersed into acetonitrile and stored for a period of one week. After this time the electrode was removed and placed in an aqueous solution and the cyclic voltammetry recorded. No significant deterioration in the aqueous voltammetric response, either in the magnitude of peak currents or peak potentials was observed.

Next cyclic voltammetry was conducted on immobilised 4-NBA in acetonitrile solutions containing either 0.1 M TBAP or 0.1 M LiClO₄ as supporting electrolyte.

Upon sweeping in a reductive direction voltammetric peaks were observed with each electrolyte salt corresponding to the reduction of the attached nitro-group moiety. With 0.1 M TBAP as supporting electrolyte a poorly resolved electrochemically reversible couple was observed at ca. -1.0 V vs. Ag. This can be attributed to the reversible one-
 5 electron reduction of the nitro-group to the corresponding radical anion. When 0.1 M LiClO₄ was used as supporting electrolyte an irreversible reduction wave was observed at ca. -0.8 V vs. Ag and a reversible system was formed on repetitive cycles at ca. -0.4 V vs. Ag.

Further cyclic voltammetric experiments were carried out using 4-NBA carbon abrasively immobilised onto a bppy electrode in acetonitrile containing 0.1 M TBAP as
 10 supporting electrolyte. The electrode was then removed from the non-aqueous solution and placed in an aqueous solution (pH 6.8). Again a stable voltammetric response was observed corresponding to the aqueous redox electrochemistry of 4-NBA. Next an electrode containing abrasively immobilised 4-NBA carbon is placed directly into the
 15 aqueous electrolyte (pH 6.8) and the voltammetry recorded. A comparison of the resulting cyclic voltammograms for both cases (with and without conducting cyclic voltammetry in non-aqueous solution prior to conducting voltammetry in pH 6.8 buffer) revealed that the magnitude of the peak currents and the peak potentials observed in the voltammetry were almost identical.

20 If the 4-NBA was physically adsorbed onto the graphite surface one would expect it to have desorbed into the acetonitrile solution, and no response would be observed either in the non-aqueous acetonitrile solution or in the aqueous electrolyte solution.

It can therefore be concluded that physical adsorption is not the mechanism by
 25 which the carbon surface of graphite or MWCNTs is modified with 4-NBA.

Example 4.2 Test for chemical adsorption (chemisorption) of 4-NBA onto graphite and MWCNTs

In previous studies chemisorption of organic molecules onto carbon is achieved
 30 in two ways. The first is an "heterogeneous" method which uses the direct electrochemical reduction of diazonium salts or the electrochemical oxidation of amines. The second method is carried out "homogeneously" (the term "homogeneous"

is used in this context to mean that both the modifier and the oxidant/reductant are in the solution phase) e.g. the reduction of aryldiazonium salts with hypophosphorous acid in the presence of graphite powder.

Barbier et al. have shown that 4-NBA can be "heterogeneously" chemically bound to the surface of a glassy carbon electrode by direct electrochemical oxidation. The mechanism of the amine bond formation to the electrode surface proceeds via the oxidation of the amine group to the corresponding radical cation, $\text{ArNH}_2^{+\bullet}$ which subsequently can react with the carbon surface to form a covalent C-N bond.

To test whether we had achieved the chemisorption of 4-NBA using a "homogeneous" method the following experiment was carried out: graphite powder and MWCNTs were derivatised with 4-NBA (10 mM in acetonitrile). Next the derivatisation procedure was repeated on fresh batches of graphite and MWCNTs with the exception that the acetonitrile was degassed with nitrogen for 20 minutes prior to use. The reaction mixture was kept under a blanket of nitrogen during the derivatisation procedure to prevent atmospheric oxygen diffusing into the solution. This prevented the possibility of aerial oxidation of 4-NBA to the radical cation by dissolved or atmospheric oxygen and subsequent reaction with the carbon material. Finally fresh batches of graphite and MWCNTs were derivatised as describe previously except that a strong oxidising agent, (tris(4-bromophenyl)aminium hexachloroantimonate (TBPAHCA, 25 mM in acetonitrile) was added to the reaction mixture. TBPAHCA was used to promote oxidation of the amine group to the corresponding radical cation and subsequent reaction with the carbon material.

The resulting 4-NBA derivatised graphite and MWCNTs from each of the three different preparations (using a strong oxidant, using acetonitrile which contained dissolved oxygen and using degassed acetonitrile) were separately immobilised onto a bppg electrode and their corresponding cyclic voltammograms recorded in pH 6.8 buffer and in acetonitrile (0.1 M TBAP). In all three cases there was no observable difference in the voltammetric behaviour of the 4-NBAcarbon or 4-NBAMWCNTs in either aqueous or non-aqueous media. It can be inferred from this result that graphite and MWCNTs are derivatised by 4-NBA in exactly the same manner whether the derivatisation is carried out in degassed acetonitrile, acetonitrile containing dissolved oxygen or in the presence of a strong oxidising agent. This implies that 4-NBA

modifies the carbon materials even when the formation of the corresponding radical cation of the amine group is unlikely to occur. Thus it can be concluded that chemical adsorption of 4-NBA via formation of the radical cation and subsequent attack of the carbon surface is not the likely mechanism of carbon modification.

5 One further possible mechanism by which the 4-NBA molecules could chemically attach themselves to the surface is by reacting with surface carboxylic acid groups, which are formed on the surface of synthetic graphite and MWCNTs during manufacture, to form the corresponding amides. This however is not plausible for two reasons. First, amides are susceptible to cleavage by hydrolysis at high and low pH,
10 whilst we have demonstrated by using cyclic voltammetry and observing a stable voltammetric response over many repeat cycles that 4-NBA remains stable on the carbon surface at pH 1.0 and pH 12.0. Second, experiments have been carried out which demonstrate that significant amounts of 4-NBA have modified the carbon surface stirring in the reaction mixture for just 40 minutes. In order for amidification to take
15 place on time scales shorter than several weeks it is customary to use a coupling agent such as dicyclohexylcarbodiimide (DCC) as a catalyst to facilitate nucleophilic attack by the amine onto the carboxylic acid and to assist in the departure of the OH⁻ leaving group. In the present derivatisation procedure there is neither a coupling agent nor sufficient time for amidification to occur.

20

Example 4.3 Test for full or partial intercalation of 4-NBA into graphite and MWCNTs: voltammetric evidence

Having established in the previous two sections of this Example that 4-NBA is unlikely to adsorb onto the surface of graphite powders or MWCNTs the inventors then
25 considered the possibility of full or partial intercalation of 4-NBA at localised edge-plane-like defects on the carbon surface. First the electrochemical evidence in light of the extensive literature devoted to the subject of graphite intercalation compounds was studied.

The fact that voltammetry can be observed in non-aqueous solutions, even after
30 soaking a 4-NBA modified electrode in acetonitrile for one week, and yet we have shown that 4-NBA is unlikely to have been physisorbed or chemisorbed onto the carbon surface, implies that there may be some partial intercalation of 4-NBA into the carbon

material. This is likely to occur at edge plane or edge-plane-like defects on the surface of either graphite or MWCNTs. Further electrochemical evidence for this stems from the effect of the supporting electrolyte used in the acetonitrile solutions.

If tetrabutylammonium perchlorate (TBAP) is used as the supporting electrolyte salt then any features in the cyclic voltammetry of 4-NBAcarbon or 4-NBAMWCNTs are small and poorly defined. However if the TBAP salt is replaced with lithium perchlorate then well-defined voltammetry is observed (figure 7). In particular it is worth noting that 4-NBA appears to remain bound to carbon in acetonitrile and does not leach into the solution phase, unless it is electrochemically reduced in the presence of Li^+ ions. When this occurs, the reduction, unlike in the case of TBAP, produces well defined peaks in the voltammetry. An investigation of the electrochemically reversible couple observed at circa -0.4 V vs. Ag reveals that upon repetitive cycles the corresponding peaks rapidly decrease and have completely disappeared by the tenth scan. If the experiment is repeated and the solution is agitated between recording the first and second scan by gently stirring the solution while the electrode is still immersed in it, the peaks associated with this redox process are no longer present in the second scan. This implies that the redox species, which is a reduced form of 4-NBA is in the solution phase and that stirring of the solution removes this species from the diffusion layer extending from the electrode surface into the bulk solution. Hence the signal corresponding to this species is no longer observed in the voltammetry after stirring.

This behaviour can be explained if 4-NBA is partially intercalated at edge-plane defect sites along the surface of the carbon. The NBu_4^+ cation may be sterically hindered from approaching and complexing with the 4-NBA molecule as it lies inside the "pocket" formed by its partial intercalation into the disordered defect site (figure 8). Furthermore, the NBu_4^+ cation typically forms weakly bound ion-pair complexes. Hence the voltammetry of 4-NBAcarbon or 4-NBAMWCNTs observed in acetonitrile containing 0.1 M TBAP is poorly defined. Lithium cations on the other hand are much smaller in size and might therefore approach the 4-NBA even when it is partially intercalated. Upon reduction of the nitro-group the lithium ions, being highly polarizing, can form a complex with the reduced form of 4-NBA as either the radical anion or the arylnitroso/arylhydroxylamine. This complexation with Li^+ ions may cause the $[\text{Li 4-NBA}]$ ion pair to leach out into solution. The formation of $[\text{Li 4-NBA}]$

ion pairs is supported by the fact that the peak potential for the reduction in 0.1 M LiClO₄ is shifted in a positive direction compared to the peak potential in 0.1 M TBAP. This positive shift in peak potential upon complexation with Li⁺ has been well documented in the literature. Initially the [Li 4-NBA] ion pair remains in the diffusion layer adjacent to the electrode surface and so further redox voltammetry can be observed. However, upon solution agitation these ion pairs can be transported into bulk solution outside the diffusion layer and thus the corresponding voltammetry is no longer observed.

The small size of the solvated Li⁺ ion is probably crucial to this process as even when the size of the quaternary ammonium cation is reduced by repeating the experiments with tetraethyl ammonium and tetramethyl ammonium perchlorates (TEAP and TMAP respectively) the voltammetry remains poorly-defined.

Full intercalation of 4-NBA deep within the inter-layer region in native (i.e. unmodified or treated) graphite or MWCNTs (which are analogous to "rolled-up" sheets of graphite) is highly unlikely. The inter-layer spacing (I_c) between ordered graphite sheets is 3.35 Å (I_c =3.44 Å in MWCNTs) which is too small to reasonably accommodate a 4-NBA molecule (figure 9). In order for full intercalation to occur the inter-layer spacing must increase. An extensive literature search reveals that: (1) there is no evidence of acetonitrile spontaneously intercalating into native graphite, thus there is no evidence for swelling of the graphite powder or MWCNTs by immersion into acetonitrile which would facilitate 4-NBA intercalation; (2) there is no evidence to suggest organic aromatic molecules similar in size to 4-NBA spontaneously intercalate into native graphite; (3) in the case of compounds of formula (I) where Y is an amine group, there is no direct evidence for amine intercalation (including ammonia and methylamine) into native graphite. However, all the above scenarios are possible when the inter-layer spacing (I_c) between graphite sheets is increased. This is readily achievable by intercalating alkali metal ions such as Li⁺, K⁺ into graphite to produce graphite intercalation compounds (GICs) e.g. C₈Li, C₂₄Li, or by using graphitic oxide, and graphitic acid. There is even evidence to suggest that SWCNTs can intercalate K⁺ and FeCl₃ without rupturing the tube structure. Hence, the present derivatisation procedure does not include any of the above systems or criteria, and it can be concluded that full intercalation of 4-NBA into graphite does not occur.

Example 4.4: Test for full or partial intercalation of 4-NBA into graphite and MWCNTs: evidence from electron microscopy and X-ray powder diffraction

5 Having inferred that intercalation may be responsible for the modification of graphite and MWCNT by 4-NBA using electrochemical means, evidence from other techniques is now presented.

10 Intercalation is only likely to occur at the edge-planes of graphite. These edge-plane surface sites are numerous on graphite powder particles and are the site of much of the chemical and electrochemical surface activity. Large regions of these edge-plane defects lead to areas of “disordered” graphite where the well-defined graphite crystal structure breaks down. Due to the relatively large dimensions of these disordered domains in graphite powder and the irregular morphology and size distribution of such particles (2-20 μm diameter) imaging of the surface before and after modification with 4-NBA using the techniques of electron microscopy does not give an insight into the nature and effect of the surface modification. However, MWCNTs have a relatively well defined size and morphology, and as such, any difference or disparity arising from modifying the surface with 4-NBA should become apparent.

20 Intercalation of 4-NBA into MWCNTs should cause some degree of expansion in the size of the spacing between adjacent graphite sheets or regions of graphitic material on the surface causing the tubes to “swell”. In extreme cases these distortions could even cause the tubes to deform and/or rupture. In order to determine whether any swelling could be observed in the 4-NBA modified MWCNTs SEM was employed to image both unmodified “native” MWCNTs and 4-NBA modified MWCNTs after abrasive immobilisation onto the surface of a bppg electrode (figure 10a and 10b). Careful analysis of the diameter of the CNTs reveals that the average diameter of the native, unmodified MWCNTs is ca. 40 nm whilst the average diameter of 4-NBAMWCNTs is ca. 60 nm (based on a sample of fifty measurements each for native and 4-NBAMWCNTs, standard deviation in both cases was ca. 10 nm).

30 Numerous research groups have devoted considerable time and effort into modelling the processes that control CNT formation and growth. A common theoretical model used to describe CNT formation using chemical vapour deposition (CVD) as a method of synthesising CNTs is the step-flow growth kinetics model. In this model

differences in the surface diffusion rates of carbon atoms along the growing nanotube wall lead to the formation of regions of multi-island nucleation in front the propagating “step” which can increase the number of surface defects and disordered “amorphous” regions. Furthermore, the intrinsic inequality of surface diffusional fluxes which feed the growth of different layers during MWCNT formation lead to “bamboo” structures. In these structures the graphite sheets are aligned at an angle to the axis of the nanotube and thus terminate at the surface of the tube as an edge-plane defect. As nearly every sheet must terminate at the surface, the number of edge-plane defects is large. One image used to describe these structures is to liken the bamboo MWCNT to a number of paper cups stacked one inside the other like so: <<<<<<< where “<” represents multiple nanotube walls.

The formation of “bamboo-MWCNTs” is temperature dependant. The MWCNTs used in this example were supplied by NanoLab Inc. They manufactured this sample using a CVD technique which operated at temperatures of ca. 900 K. Theoretical models predict that some multi-island nucleation and the subsequent formation of bamboo-like regions along the MWCNTs is likely to occur in this temperature region.

It is postulated that it is the presence of these bamboo-like regions along the MWCNTs that is responsible for the large uptake of 4-NBA and the resulting large currents passed during the voltammetric experiments conducted on them.

In order to provide us with a further insight into the morphology of the MWCNTs, HRTEM imaging was carried out. Figure 11a and 11b show the HRTEM images of a sample of MWCNTs. These images indicate that both “bamboo-like” structures (see below) and hollow-tube structures occupy the length of a MWCNT.

The discovery of “bamboo-like” regions along the MWCNTs provides a possible explanation for the relatively large (milli-Ampere) currents passed during reduction/oxidation of 4-NBA on carbon and especially 4-NBAMWCNTs. These large currents imply that the coverage of 4-NBA on the graphite particles and MWCNTs is high. If 4-NBA is indeed partially intercalating into edge-plane defects on the MWCNTs then these defect sites must be so numerous that they can not simply be located at the open ends of the nanotubes, but along their surfaces too.

Next X-ray powder diffraction (XPD) was used to examine the effect of modifying graphite powder and MWCNTs with 4-NBA. The fundamental equation used to analyse X-ray diffraction data is given by Bragg's law, equation (2):

$$n\lambda = 2nd \sin \theta \quad (2)$$

5 where n is an integer representing the order of reflection from a set of planes, λ is the wavelength of X-ray radiation / Å, d is the inter-plane spacing / Å, and θ is the angle of incidence at which the X-ray radiation falls on the sample. Any increase in the inter-layer spacing due to intercalation of 4-NBA into the lattice increases the value of d and thus can be observed by comparing the diffractogram of the modified sample with the
10 diffractogram of the unmodified sample.

The X-ray powder diffractograms of 4-NBA carbon and unmodified graphite powder were recorded. Comparison of the diffractograms showed no qualitative or quantitative differences, either in the position of the peak or in the peak width and shape. Both samples produced a value for the inter-layer spacing of 3.37 ± 0.01 Å
15 which is in good agreement with literature values of 3.35 ± 0.05 Å. This result excludes the possibility of full intercalation of 4-NBA into the graphite lattice. However this does not exclude the possibility of partial intercalation of 4-NBA at the disordered sites containing edge plane steps and defects. This is because XPD can only be used to interrogate highly ordered regions possessing a well defined crystal structure from
20 which to obtain reflected X-rays at well defined values of θ . Any disordered regions simply scatter the X-rays at random θ values without constructively interfering and hence these signals are lost as noise. Due to the much more ordered morphology of MWCNTs compared to graphite powder particles a comparison of 4-NBAMWCNTs and native MWCNTs using XPD is much more instructive as to the nature of the
25 surface modification by 4-NBA.

To this purpose, X-ray powder diffractograms of 4-NBAMWCNTs and "native" unmodified MWCNTs were recorded for comparison (figure 12). The first point to mention is that the peak position for both the modified and unmodified MWCNTs is identical within experimental error and corresponds to an inter-layer separation of 3.47 ± 0.04 Å which is again consistent with the literature value of 3.44 ± 0.04 Å. The
30 second point to note is in both cases the peaks are broadened and are unsymmetrical with a "tail" on the left hand edge of each peak. This is effect is due to variations in the

inter-layer spacings leading to a certain degree of disorder in the crystal structure of the nanotubes. What is important to note is that the 4-NBAMWCNT peak is considerably broader than the native MWCNT peak. Analysis of the normalised peaks reveals that the full-height-half-width of the native MWCNT peak is 0.9446, whilst the 4-NBAMWCNTs full-height-half-width value has increased by nearly forty percent to 1.3855. This shows that there has been considerable disruption and an increase in the disorder of the MWCNT structure which may provide supporting evidence for partial intercalation of 4-NBA molecules at the edge-plane surface defects. The increase in disordering between the graphite sheets can be measured quantitatively using the Scherrer equation (3) which relates the half-height-full-peak-width to the average number of planes present in the ordered part of the crystal from which the X-ray reflections occur:

$$t = \frac{0.9\lambda}{\beta \cos \theta} \quad (3)$$

$$\text{and} \quad t = md \quad (4)$$

where λ and θ are defined as per equation (2) above, β is the full-height-half-peak width, and t is the thickness of the crystalline region. Hence if the interlayer spacing (d) is known then the number of layers (m , graphite sheets in this case) in the crystalline, ordered region can be calculated from (4). Table 1 lists the data obtained from the XPD of 4-NBAMWCNTs and native MWCNTs for comparison. The value of $m = 9$ ordered layers of graphite sheets for native MWCNTs is in agreement with HRTEM studies of the MWCNTs which found an average of 9 concentric tube walls present. This value has decreased on modifying the CNTs with 4-NBA to $m = 6$ which is not an unreasonable value as it is likely that edge plane defects could expose up to the first three graphite layers.

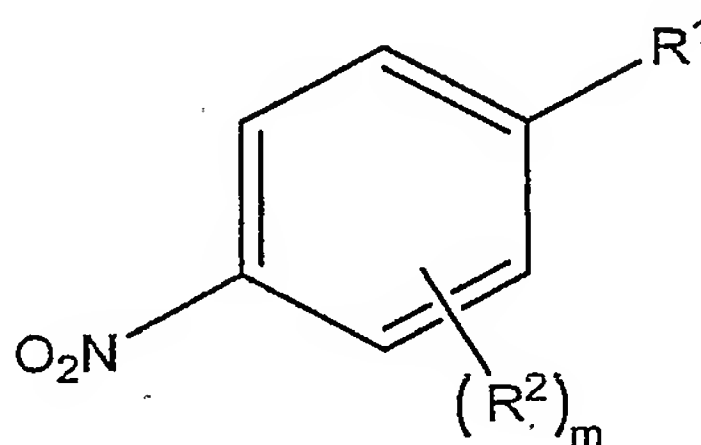
Table 1

A comparison of the experimentally determined X-ray diffraction data for unmodified native MWCNTs and 4-NBA modified CNTs:

	Inter-layer spacing / Å	Full-height-half-width / degrees	m-value, the number of adjacent ordered layers in the crystalline regions
Native MWCNT	3.47	0.9446	9
4-NBAMWCNT	3.47	1.3855	6

CLAIMS:

1. A method of modifying carbon by the partial intercalation of a compound which is a nitrobenzene derivative of formula (I):



(I)

wherein

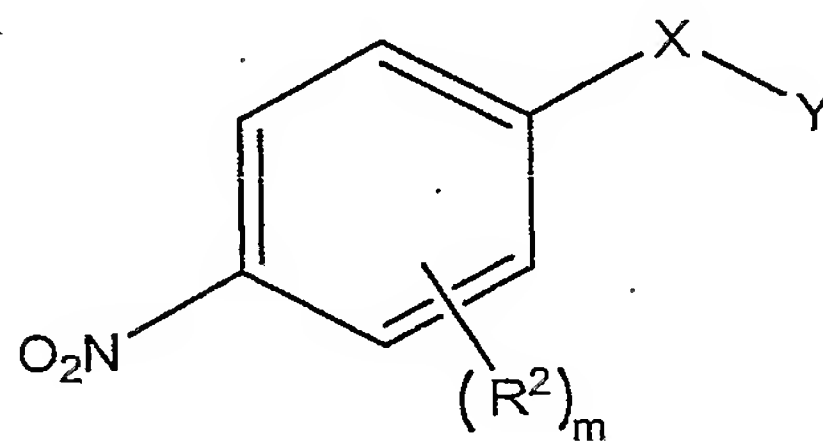
- R^1 represents a group of formula $-Y$ or $-X-Y$ wherein Y is selected from hydrogen, hydroxy, C_{1-4} alkyl and $-NR^3R^4$ wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy, and wherein X represents a group of formula $-(CR^5R^6)_n-$ wherein n is 0 or an integer from 1 to 4 and R^5 and R^6 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl, C_{1-4} alkoxy or R^5 and R^6 together form a group of formula $=O$ or $=NR^7$ wherein R^7 is selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy;
- R^2 is selected from hydroxy, halogen, C_{1-4} alkyl, C_{2-4} alkenyl, C_{1-4} alkoxy, C_{2-4} alkenyloxy, amino, C_{1-4} alkylamino, di(C_{1-4} alkyl)amino; C_{1-4} alkylthio, C_{2-4} alkenylthio, nitro, cyano, $-O-CO-R'$, $-CO-O-R'$, $-CO-NR'R''$, $-COR'$, $-S(O)R'$ and $-S(O)_2R'$, wherein each R' and R'' is the same or different and represents hydrogen, C_{1-4} alkyl or C_{2-4} alkenyl; and
- m is 0 or an integer from 1 to 4;

or a salt thereof, which method comprises mixing powdered carbon with a compound as defined above for a time sufficient to allow the compound to partially intercalate within the carbon, and isolating the resulting modified carbon.

2. The method of claim 1 wherein the powdered carbon and compound are mixed in a solvent, said solvent being an aprotic organic solvent.

3. The method of any one of the preceding claims wherein the powdered carbon is in the form of graphite or multi-walled carbon nanotubes.

5 4. The method of any one of the preceding claims wherein the compound is a nitrobenzene derivative of formula (II):



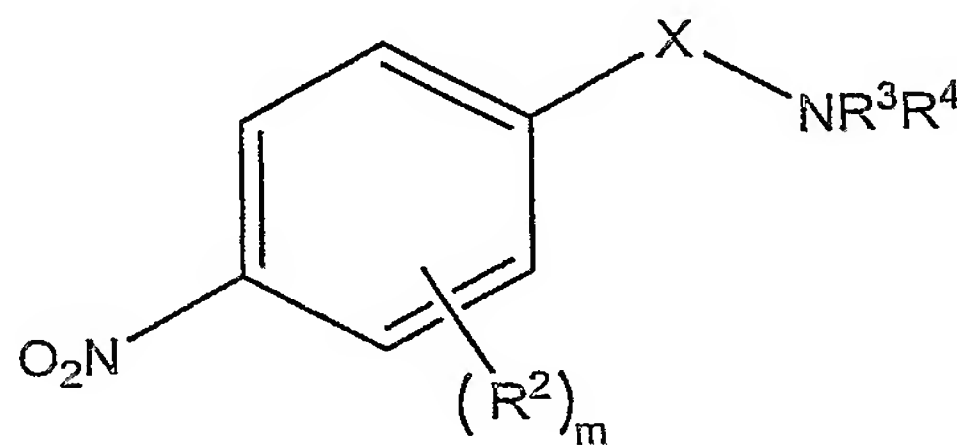
(II)

wherein:

- 10 - R^2 is selected from hydroxy, halogen, C_{1-4} alkyl and C_{1-4} alkoxy;
- m is 0, 1 or 2;
- X represents a group of formula $-(\text{CR}^5\text{R}^6)_n-$ wherein n is 0, 1 or 2 and R^5 and R^6 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy; and
- 15 - Y is selected from hydrogen, hydroxy, C_{1-4} alkyl and $-\text{NR}^3\text{R}^4$ wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy,

or a salt thereof.

20 5. The method of claim 4 wherein the compound is a nitrobenzene derivative of formula (III):



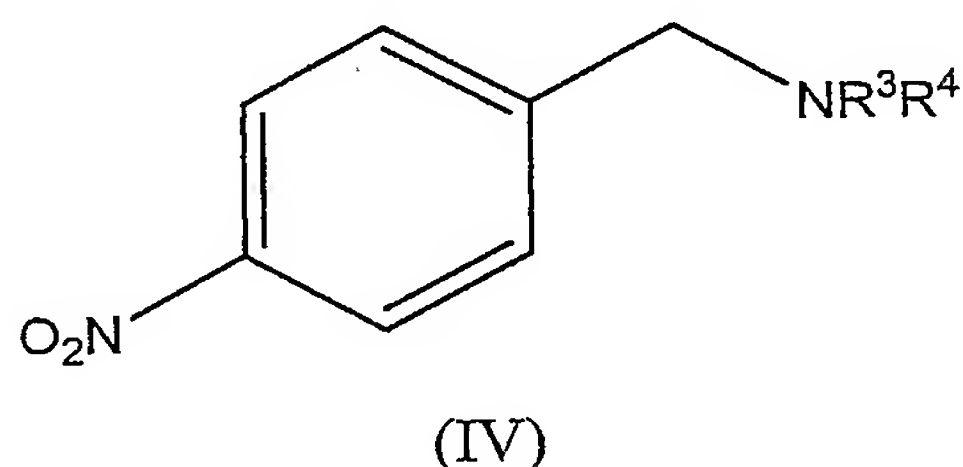
(III)

wherein:

- 25 - R^2 is selected from hydroxy, halogen, C_{1-4} alkyl and C_{1-4} alkoxy;

- m is 0, 1 or 2;
 - X represents a group of formula $-(CR^5R^6)_n-$ wherein n is 0, 1 or 2 and R^5 and R^6 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy; and
 - 5 - R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy,
- or a salt thereof.

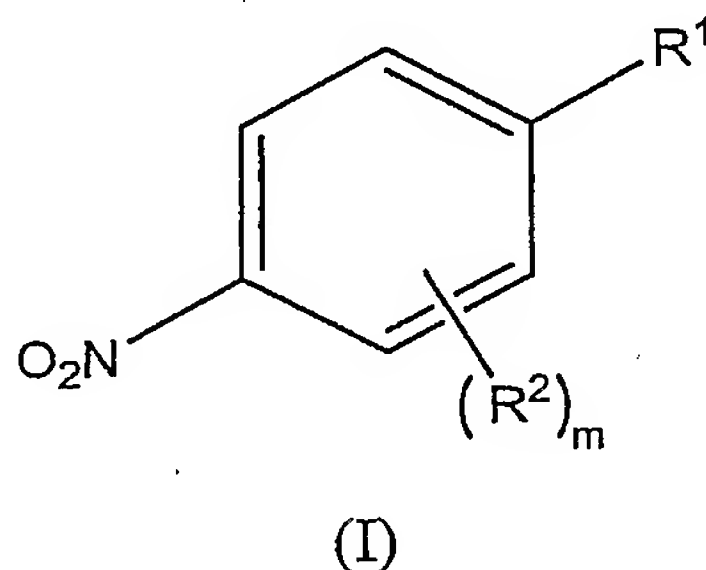
6. The method of claim 5 wherein the compound is a nitrobenzene derivative of
10 formula (IV):



wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy, or a salt thereof.

15

7. Modified carbon produced according to the method of any one of claims 1 to 6.
8. A composition comprising carbon and a compound of formula (I):



20

wherein

- R^1 represents a group of formula $-Y$ or $-X-Y$ wherein Y is selected from hydrogen, hydroxy, C_{1-4} alkyl and $-NR^3R^4$ wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy, and wherein X represents a group of formula $-(CR^5R^6)_n-$ wherein n is 0 or an integer from 1 to 4 and R^5 and R^6 are the same or
- 25

different and are selected from hydrogen, hydroxy, C₁₋₄ alkyl, C₁₋₄ alkoxy or R⁵ and R⁶ together form a group of formula =O or =NR⁷ wherein R⁷ is selected from hydrogen, hydroxy, C₁₋₄ alkyl and C₁₋₄ alkoxy;

5 - R² is selected from hydroxy, halogen, C₁₋₄ alkyl, C₂₋₄ alkenyl, C₁₋₄ alkoxy, C₂₋₄ alkenyloxy, amino, C₁₋₄ alkylamino, di(C₁₋₄ alkyl)amino; C₁₋₄ alkylthio, C₂₋₄ alkenylthio, nitro, cyano, -O-CO-R', -CO-O-R', -CO-NR'R'', -COR', -S(O)R' and -S(O)₂R', wherein each R' and R'' is the same or different and represents hydrogen, C₁₋₄ alkyl or C₂₋₄ alkenyl;
10 and

- m is 0 or an integer from 1 to 4;

or salts thereof, wherein said compound of formula (I) is partially intercalated within the carbon.

15 9. A composition according to claim 8 wherein the carbon is in the form of graphite or multi-walled carbon nanotubes.

10. A composition according to any one of claims 8 or 9 wherein the compound of formula (I) is as defined in any one of claims 4 to 6.

20

11. An electrode for use in an electrochemical sensor, said electrode comprising, disposed on a substrate, the composition as claimed in any one of claims 8 to 10 or as produced by the method of any one of claims 1 to 7.

25 12. An electrochemical sensor comprising a working electrode and a counter electrode, wherein the working electrode comprises an electrode as claimed in claim 11.

13. A sensor according to claim 12 further comprising a reference electrode.

30 14. A method for preparing an electrode for use in an electrochemical sensor, said method comprising providing a substrate and applying a composition as claimed in any

one of claims 8 to 10 or as produced by the method of any one of claims 1 to 7 to the surface of said substrate.

15. The method of claim 14 wherein the step of applying comprises abrasively
5 immobilising the composition on the surface of the substrate.

16. Use of a compound of formula (I) as defined in claim 1 in the manufacture of a composition comprising carbon, wherein said compound of formula (I) is partially intercalated within the carbon.

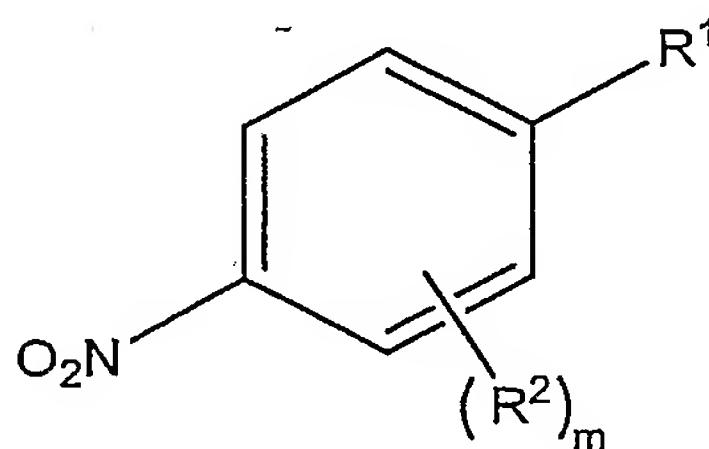
10

17. Use according to claim 16 wherein the carbon is in the form of graphite or multi-walled carbon nanotubes.

15

18. Use according to claim 17 wherein the carbon is in the form of multiwalled nanotubes.

19. Use, in an electrode, of carbon having partially intercalated within it a compound of formula (I):



(I)

20

wherein

25

R^1 represents a group of formula $-\text{Y}$ or $-\text{X}-\text{Y}$ wherein Y is selected from hydrogen, hydroxy, C_{1-4} alkyl and $-\text{NR}^3\text{R}^4$ wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy, and wherein X represents a group of formula $-(\text{CR}^5\text{R}^6)_n-$ wherein n is 0 or an integer from 1 to 4 and R^5 and R^6 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl, C_{1-4} alkoxy or R^5 and R^6 together form a group of formula $=\text{O}$ or $=\text{NR}^7$

wherein R^7 is selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy;

- R^2 is selected from hydroxy, halogen, C_{1-4} alkyl, C_{2-4} alkenyl, C_{1-4} alkoxy, C_{2-4} alkenyloxy, amino, C_{1-4} alkylamino, di(C_{1-4} alkyl)amino; C_{1-4} alkylthio, C_{2-4} alkenylthio, nitro, cyano, $-O-CO-R'$, $-CO-O-R'$, $-CO-NR'R''$, $-COR'$, $-S(O)R'$ and $-S(O)_2R'$, wherein each R' and R'' is the same or different and represents hydrogen, C_{1-4} alkyl or C_{2-4} alkenyl; and
- m is 0 or an integer from 1 to 4.

10

20. Use according to claim 19 wherein the compound of formula (I) is as defined in any one of claims 4 to 6.

21. Use of an electrode according to claim 11 in an electrochemical sensor.

15

22. Use according to claim 21 wherein the sensor is a pH sensor.

20

23. An agglomerate for use in an electrochemical sensor, said agglomerate comprising modified multiwalled carbon nanotubes dispersed in a binder, wherein the binder is a redox active material and the modified multiwalled carbon nanotubes are as defined in any one of claims 7 to 10 or are produced by the method of any one of claims 1 to 6.

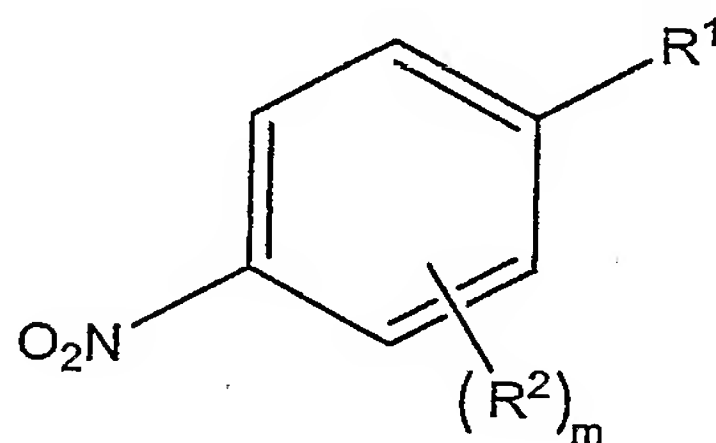
25

24. Carbon which has a compound of formula (I) partially intercalated within it and which is substantially as hereinbefore described.

ABSTRACTMODIFIED CARBON

5

There is provided a method of chemically modifying carbon comprising contacting carbon with a compound which is a nitrobenzene derivative of formula (I):



(I)

10 wherein R^1 , R^2 and m are as herein defined or a salt thereof. The modified carbon is of use in the manufacture of electrodes and electrochemical sensors.

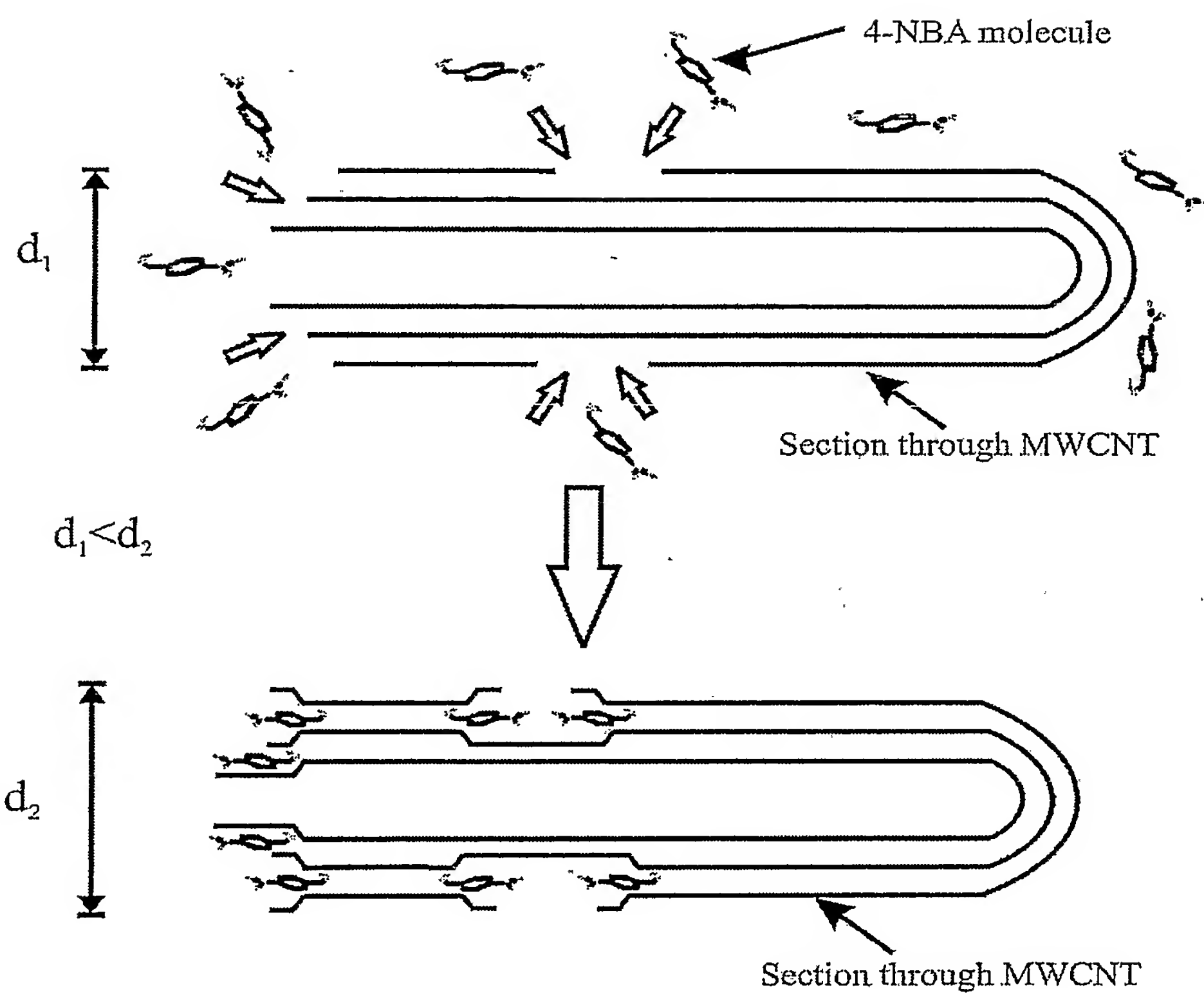


Figure 1

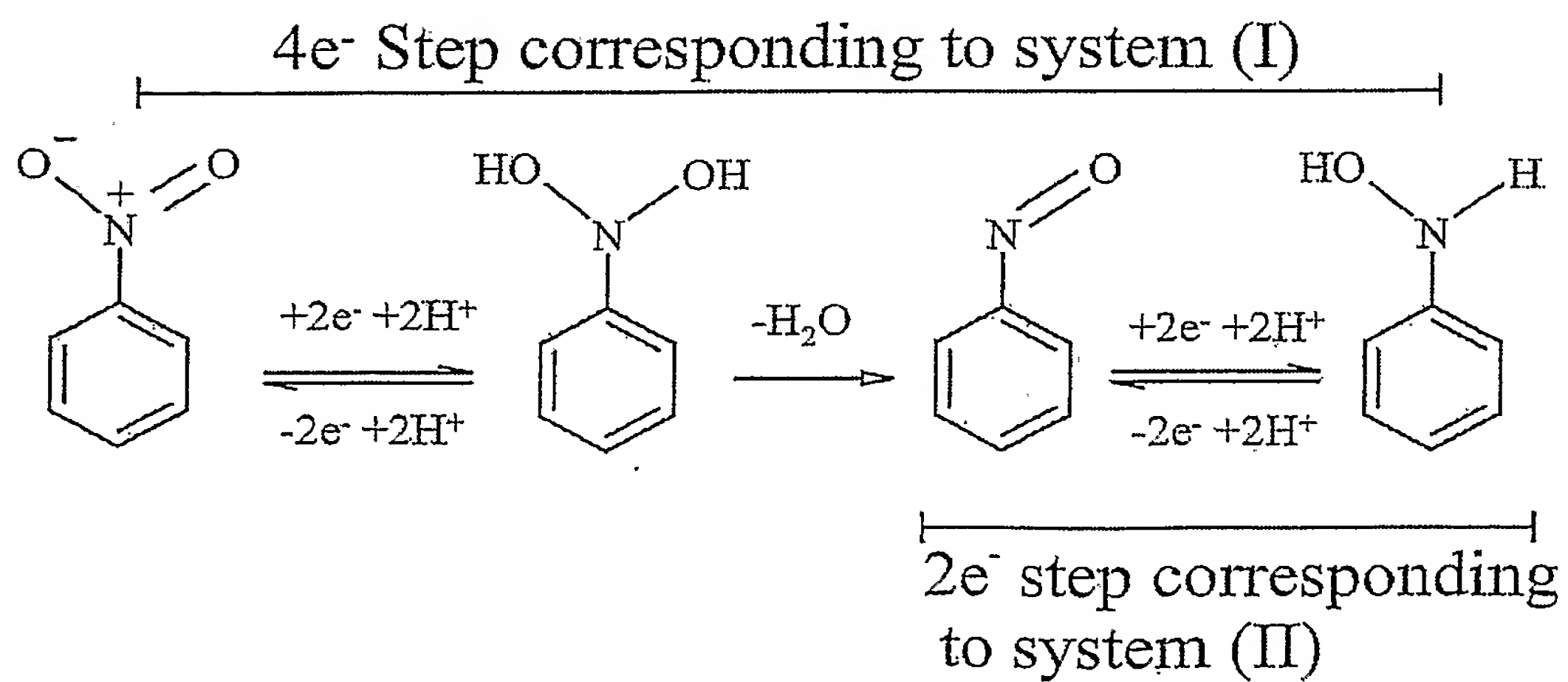
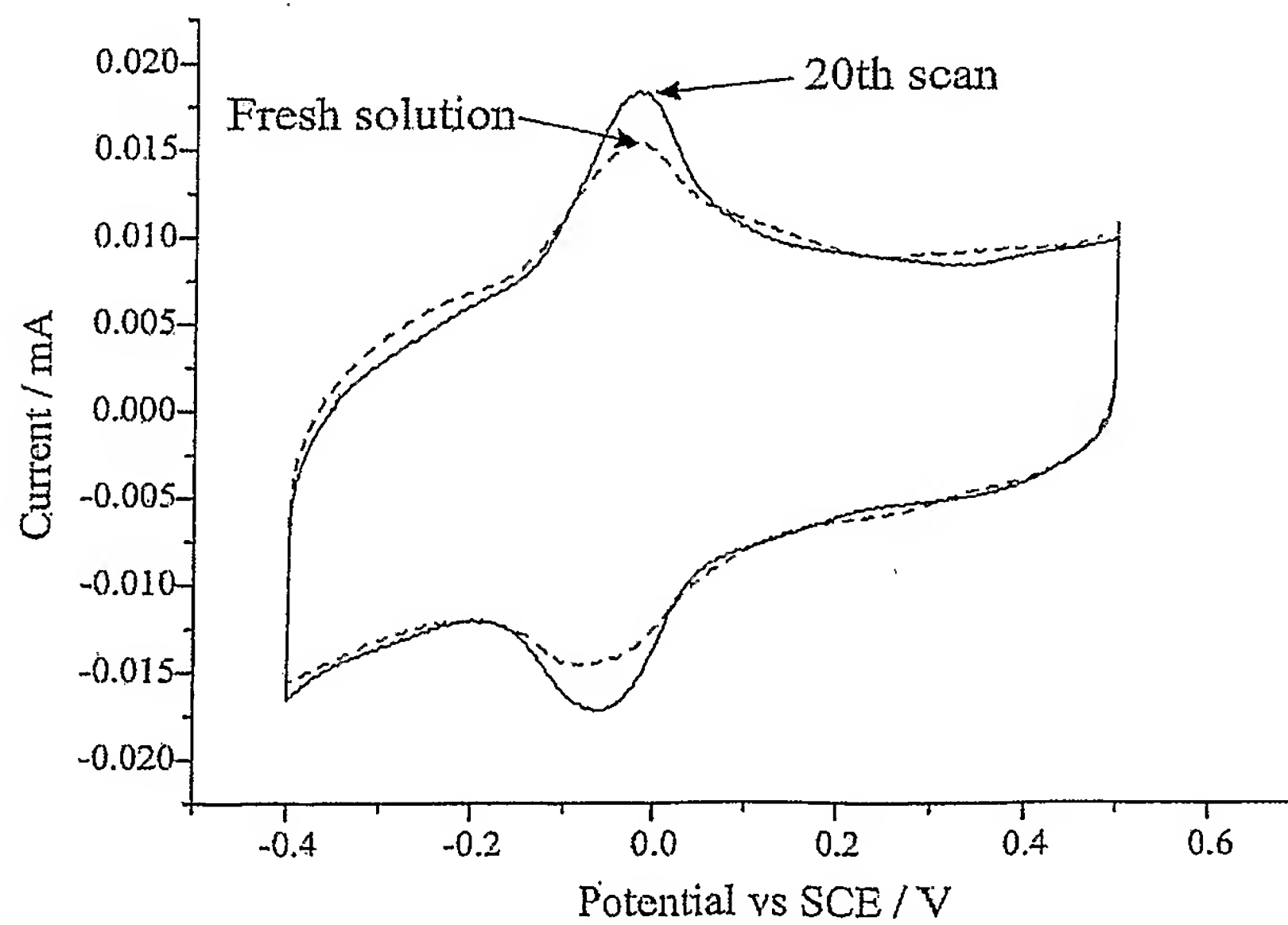
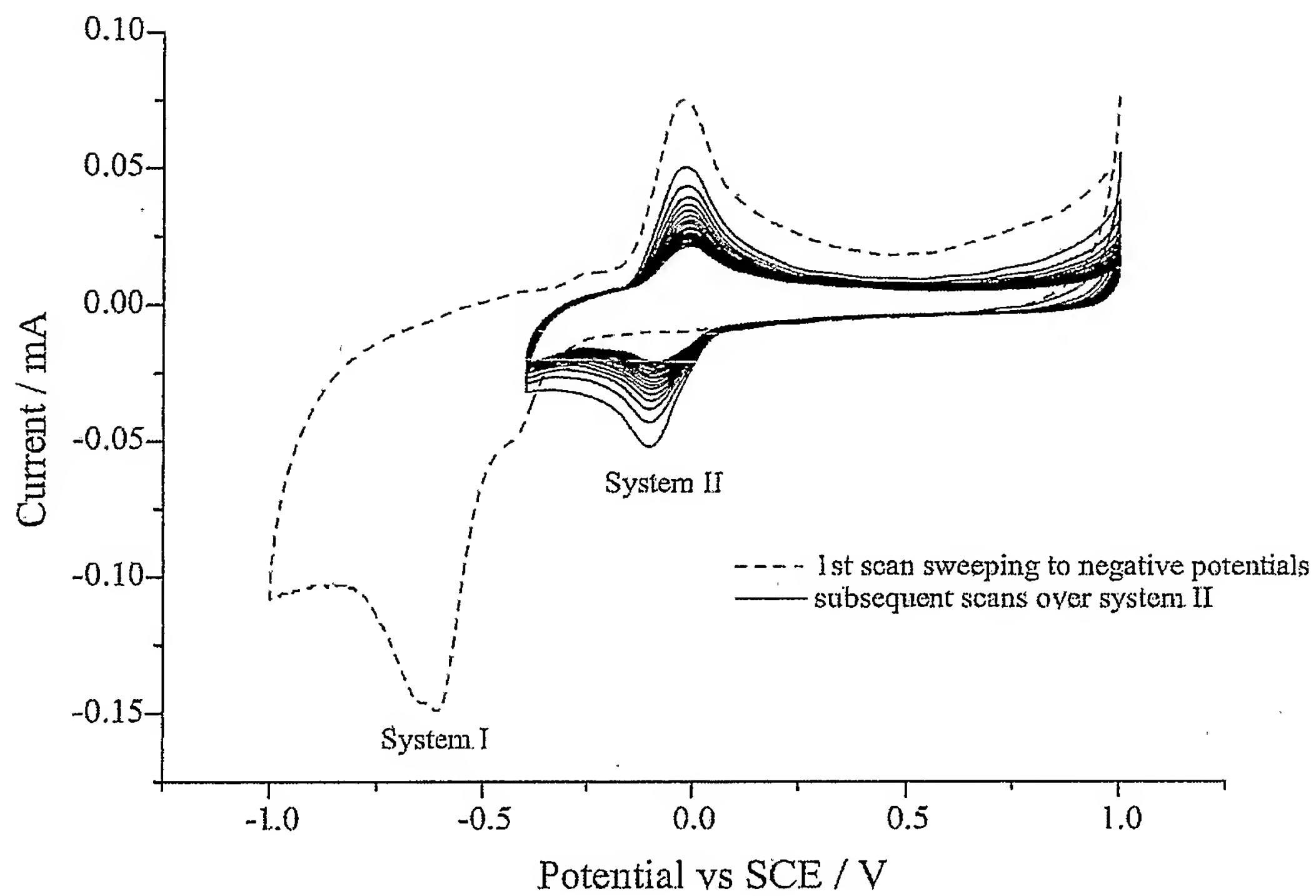


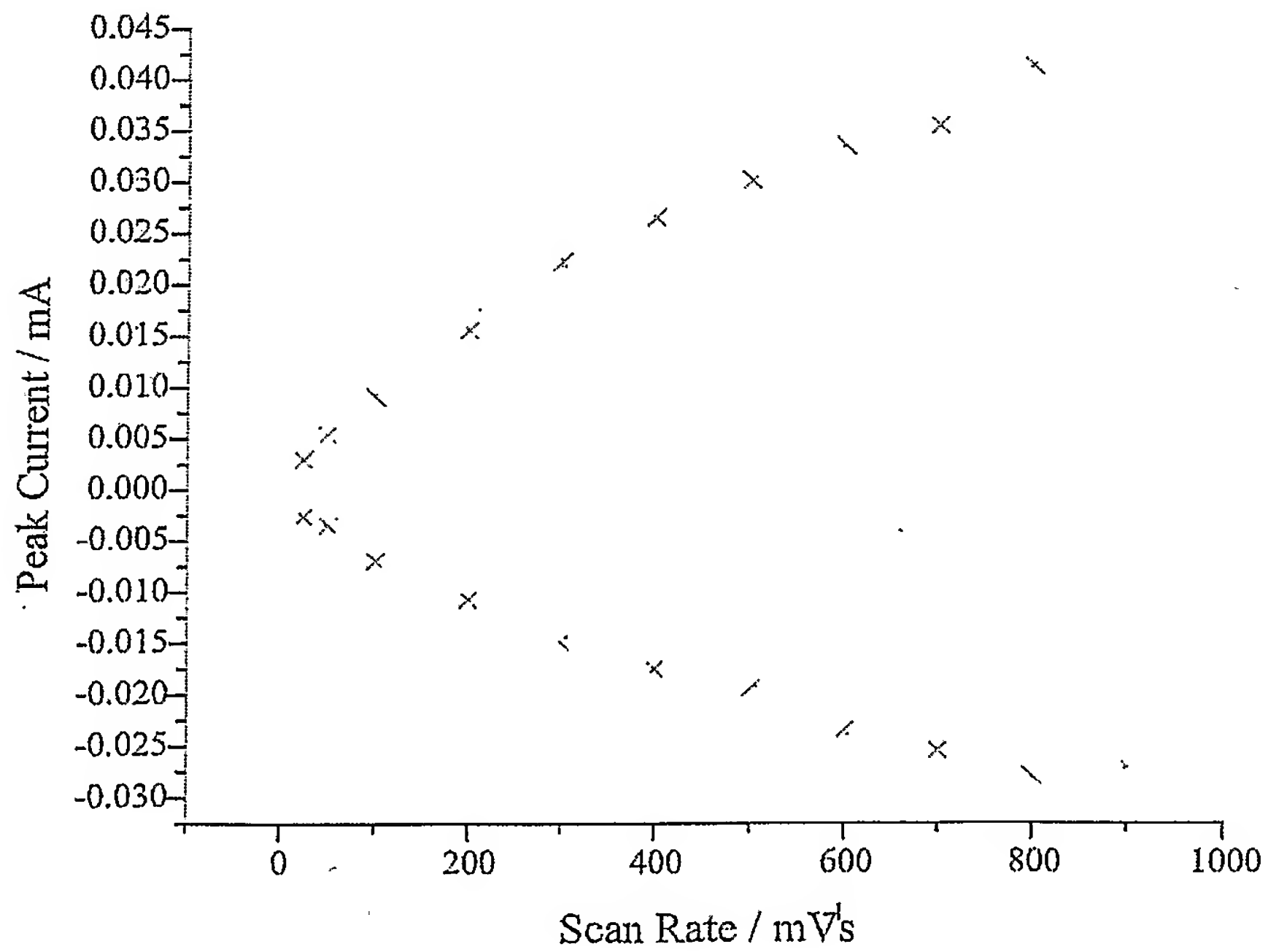
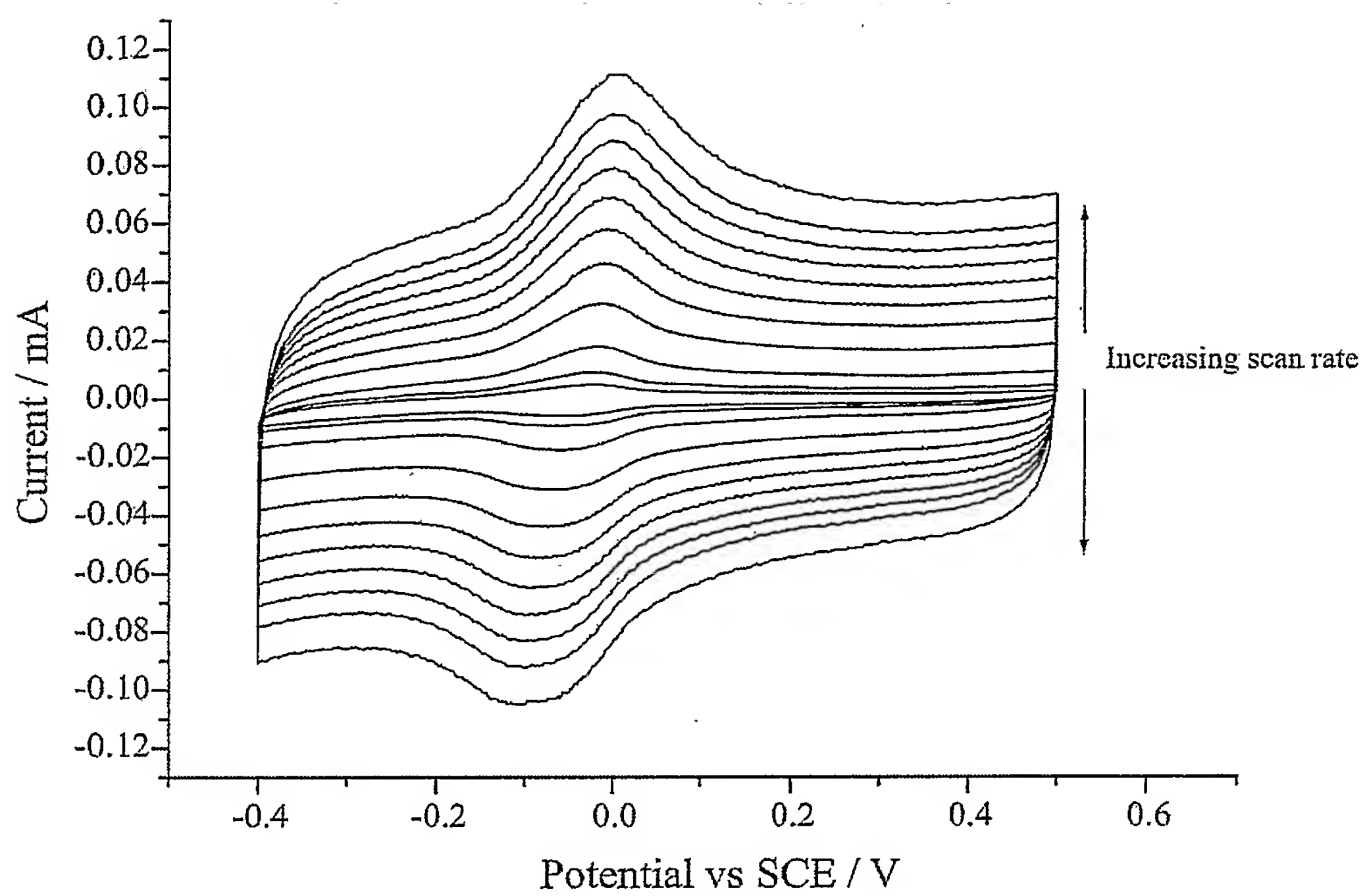
Figure 2



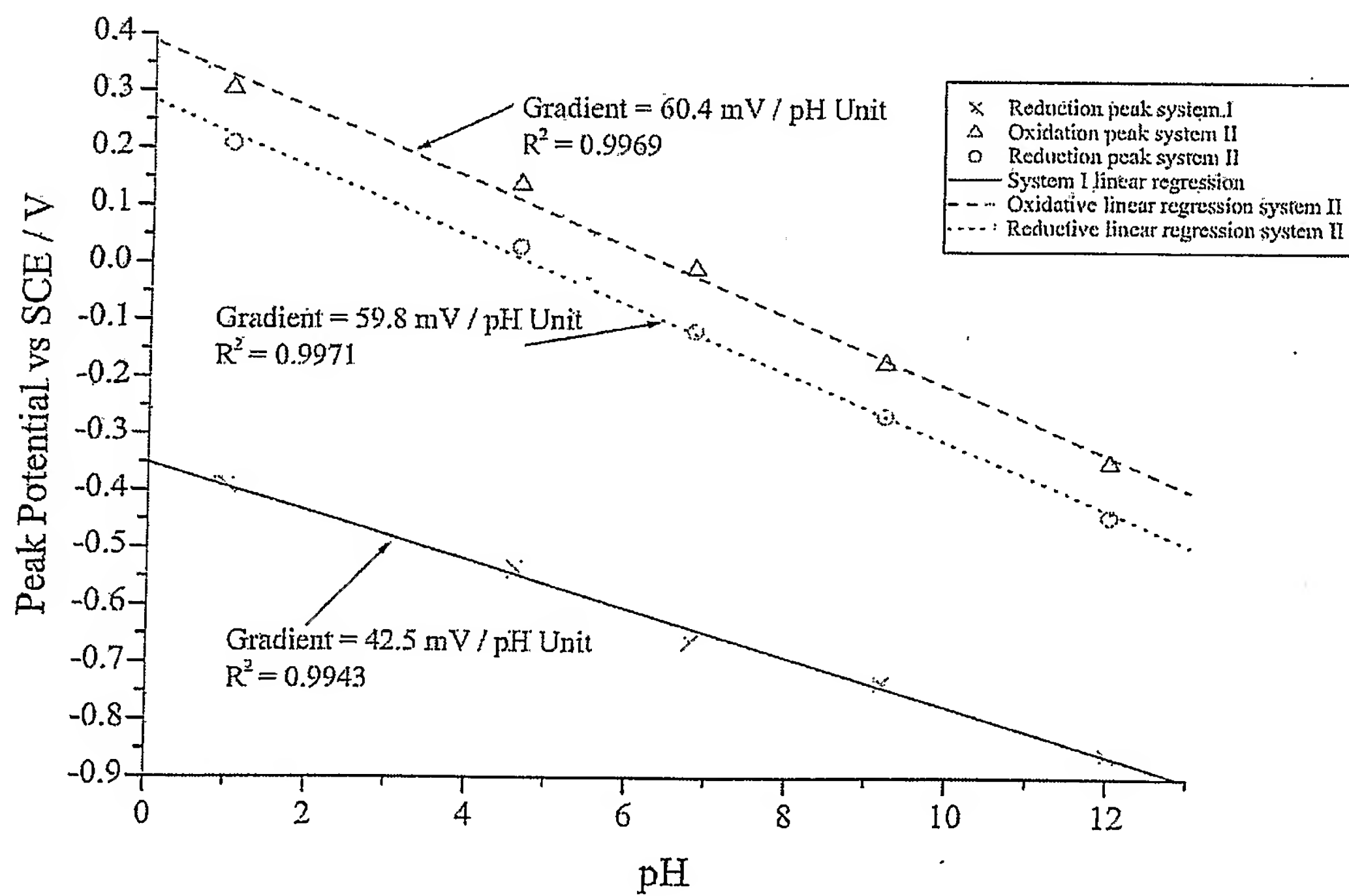
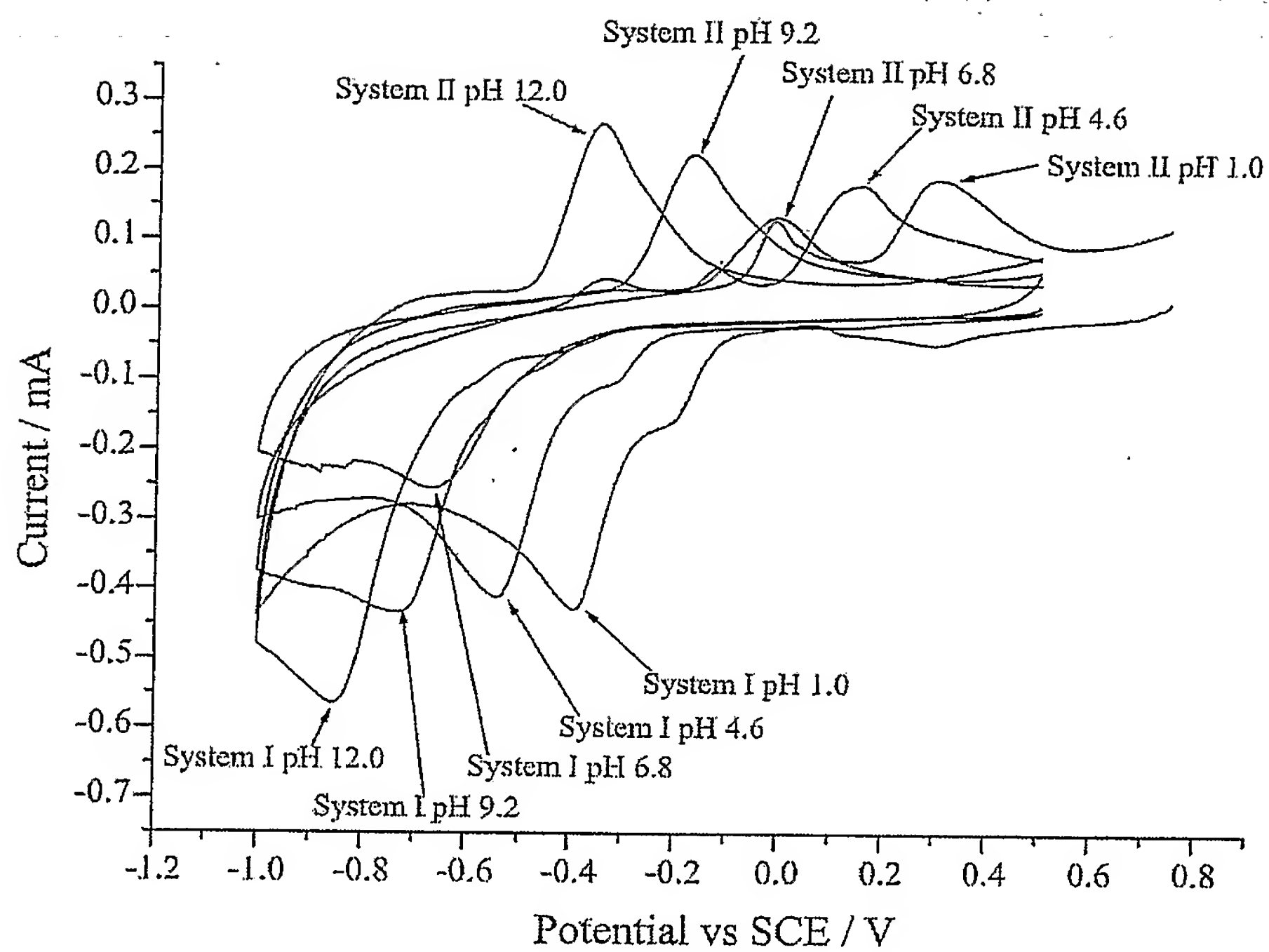


Figures 3a (top) and 3b (bottom)



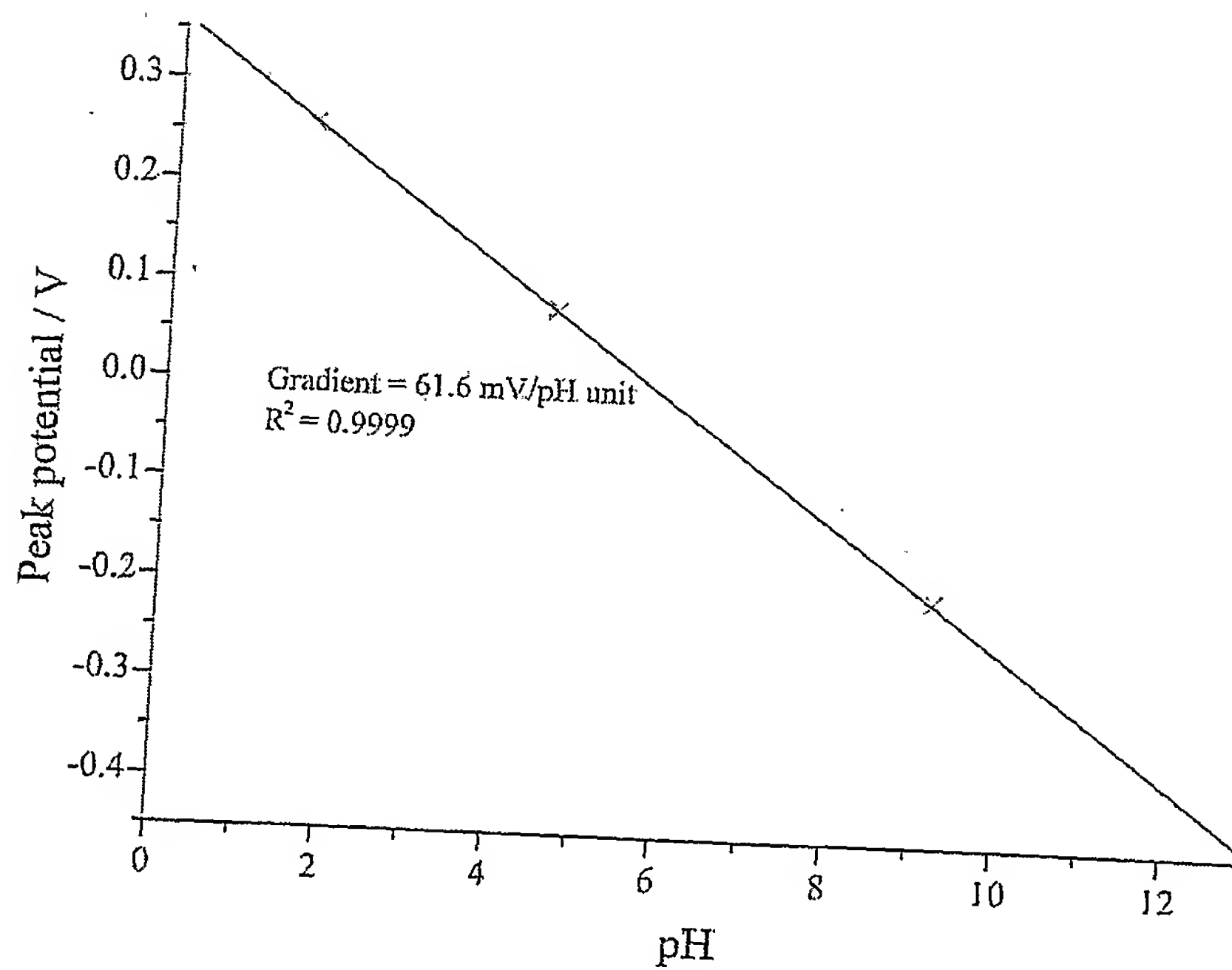
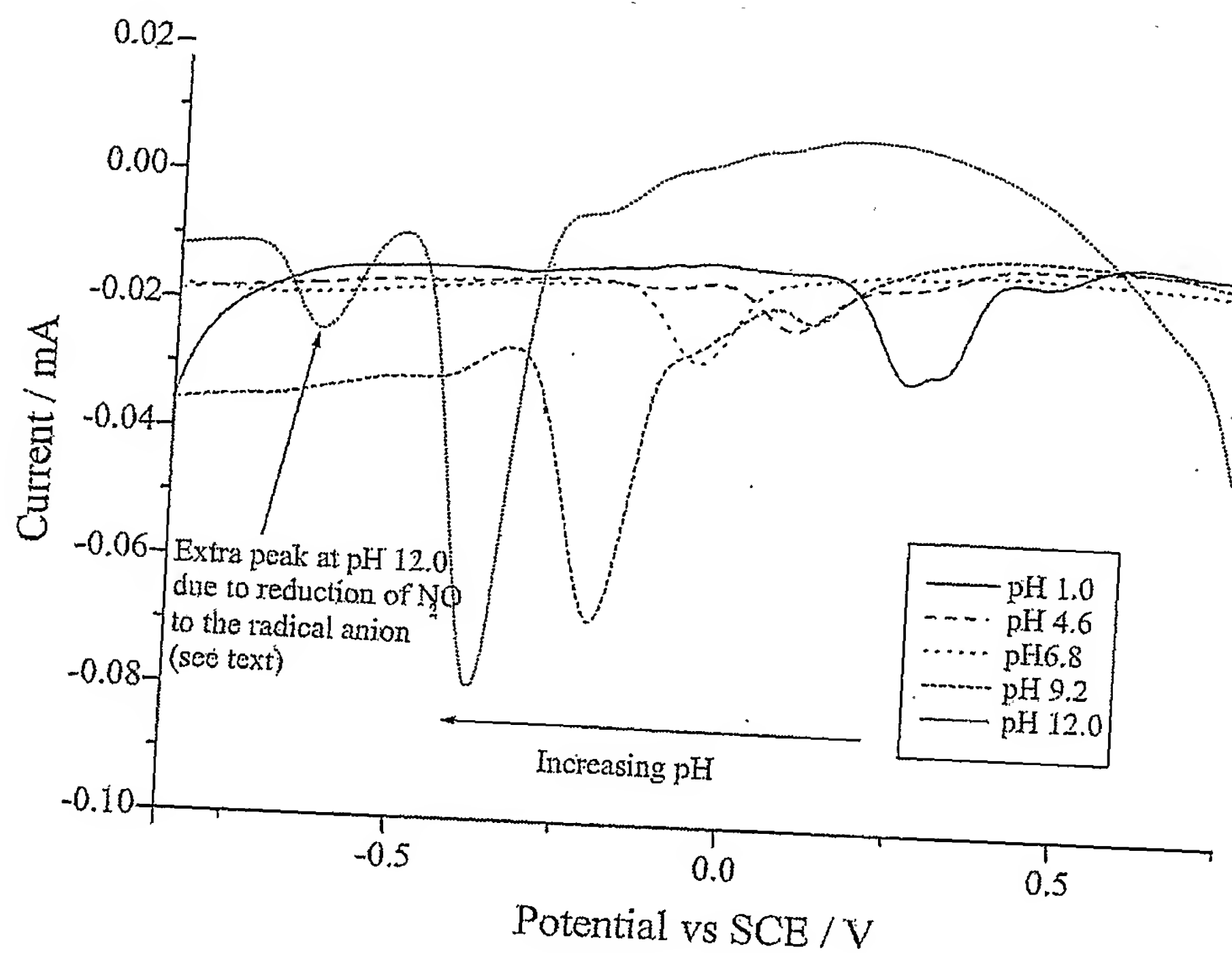


Figures 3c (top) and 3d (bottom)



Figures 4a (top) and 4b (bottom)





Figures 5a (top) and 5b (bottom)



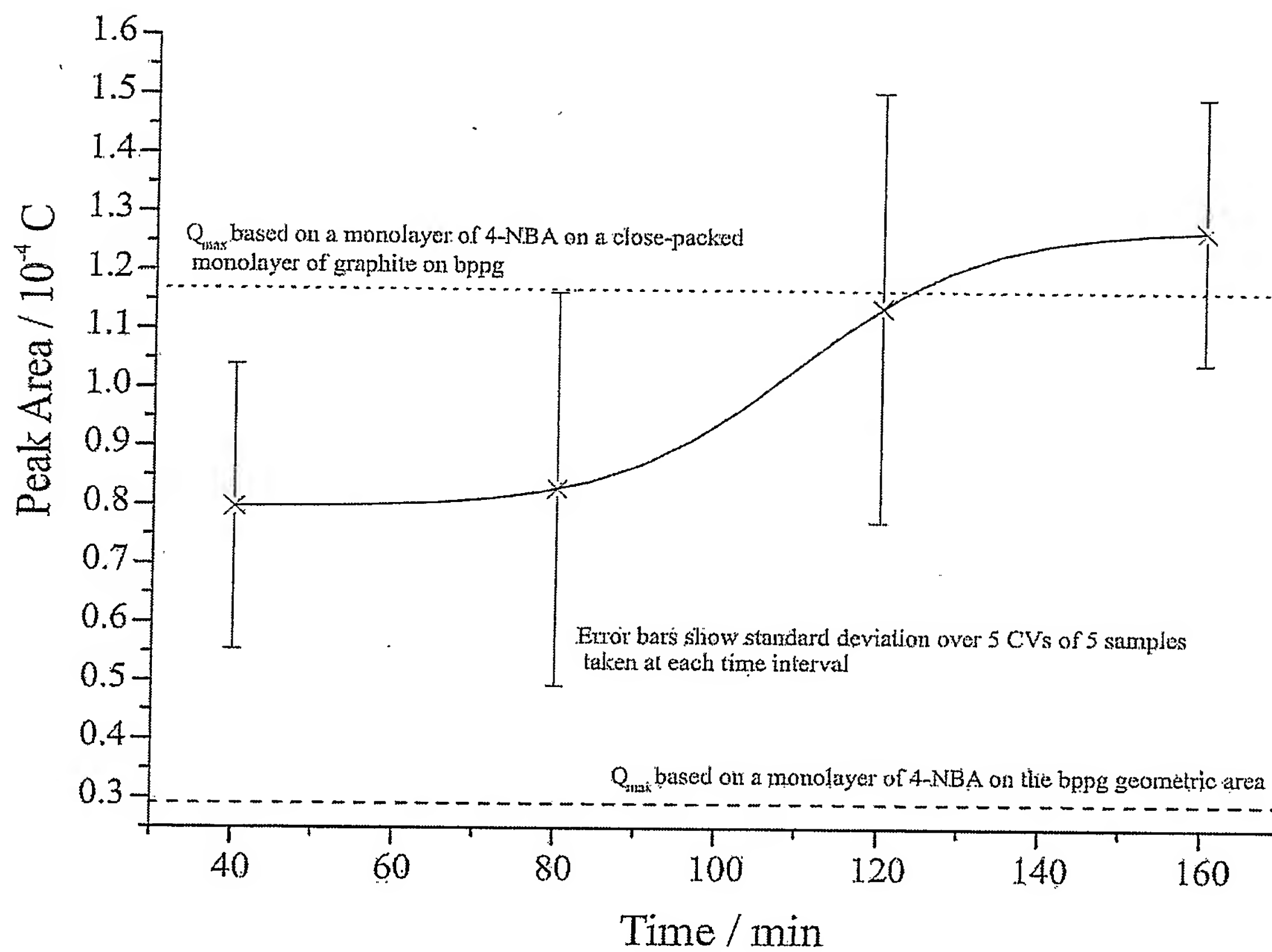


Figure 6



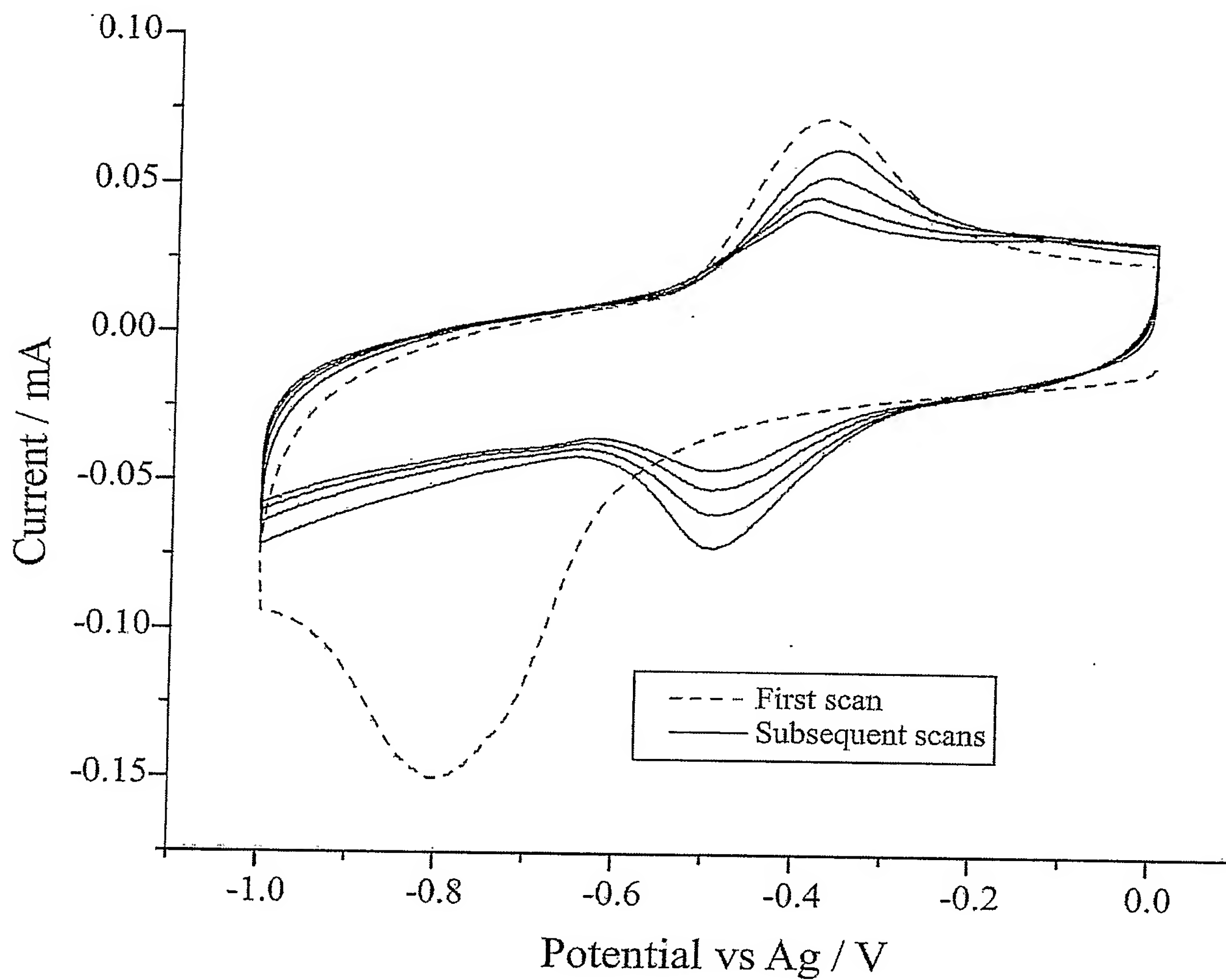


Figure 7

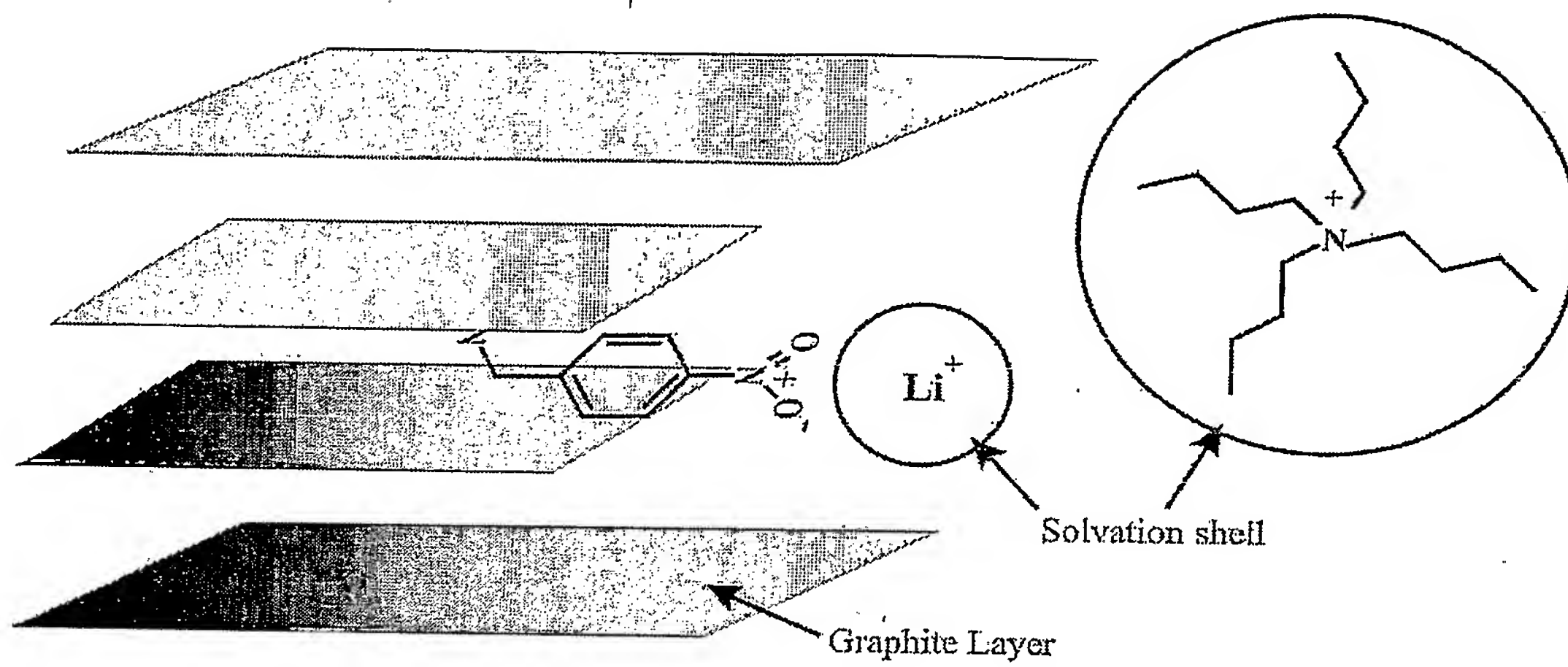


Figure 8

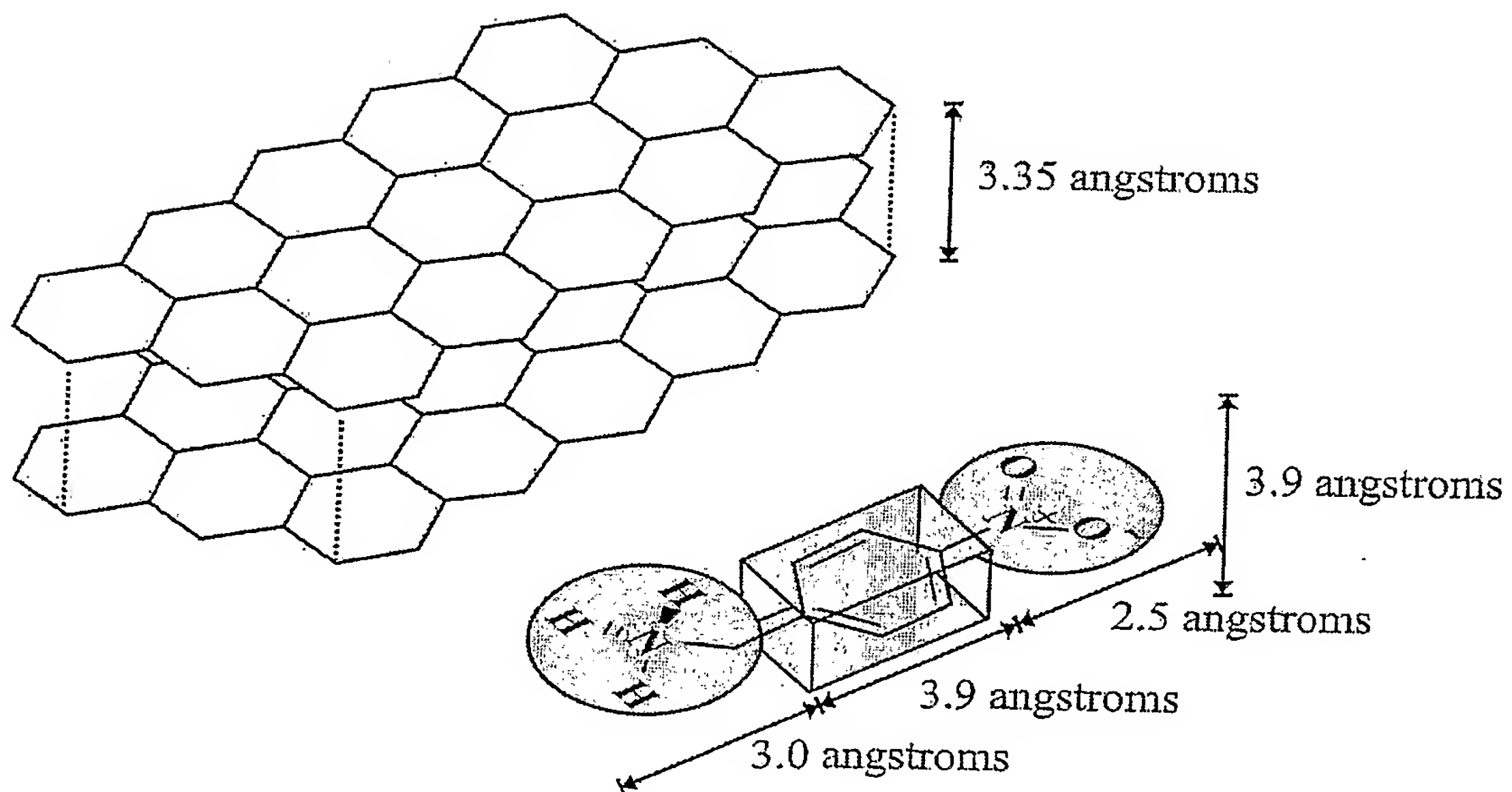


Figure 9

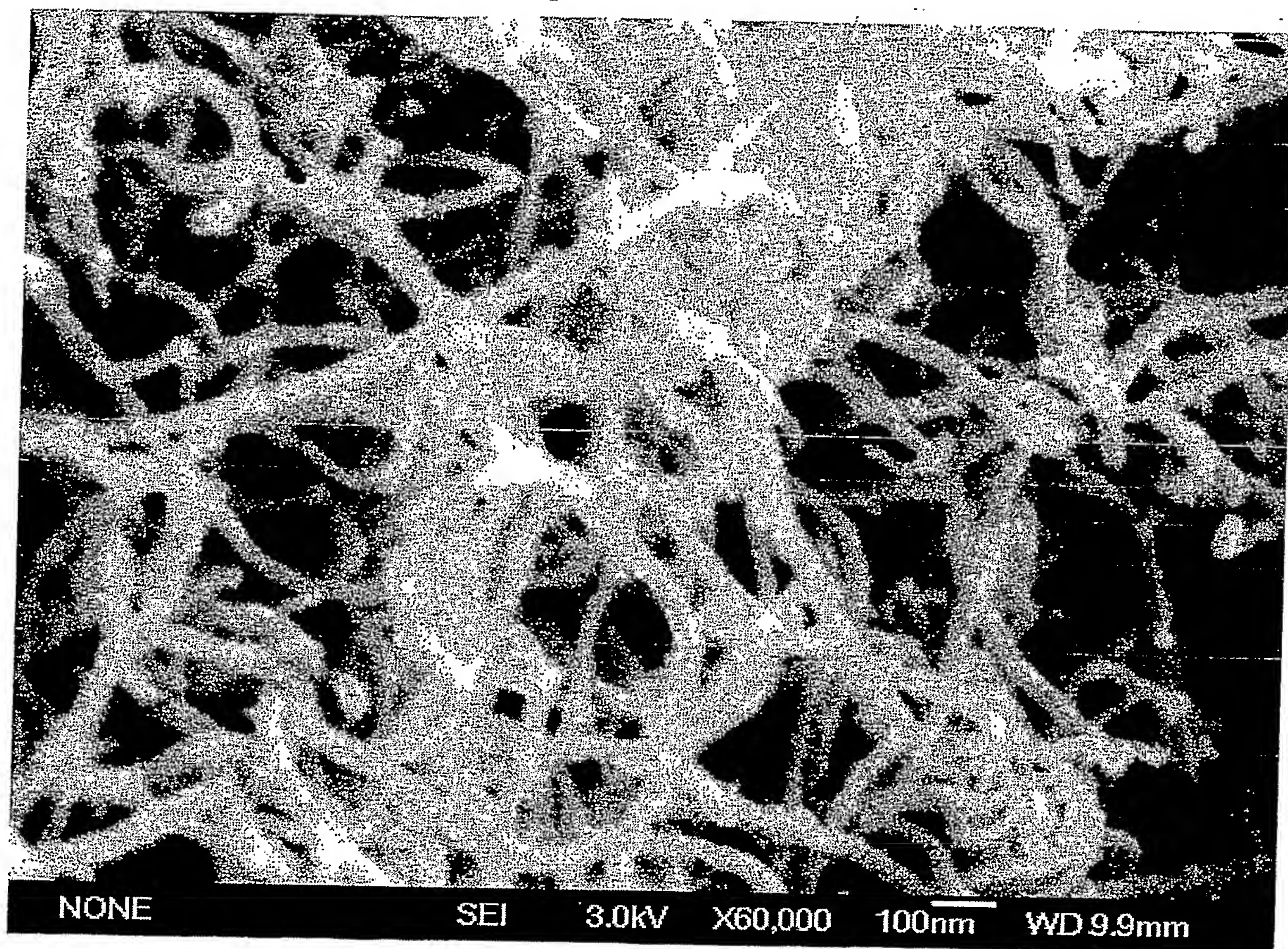


Figure 10a

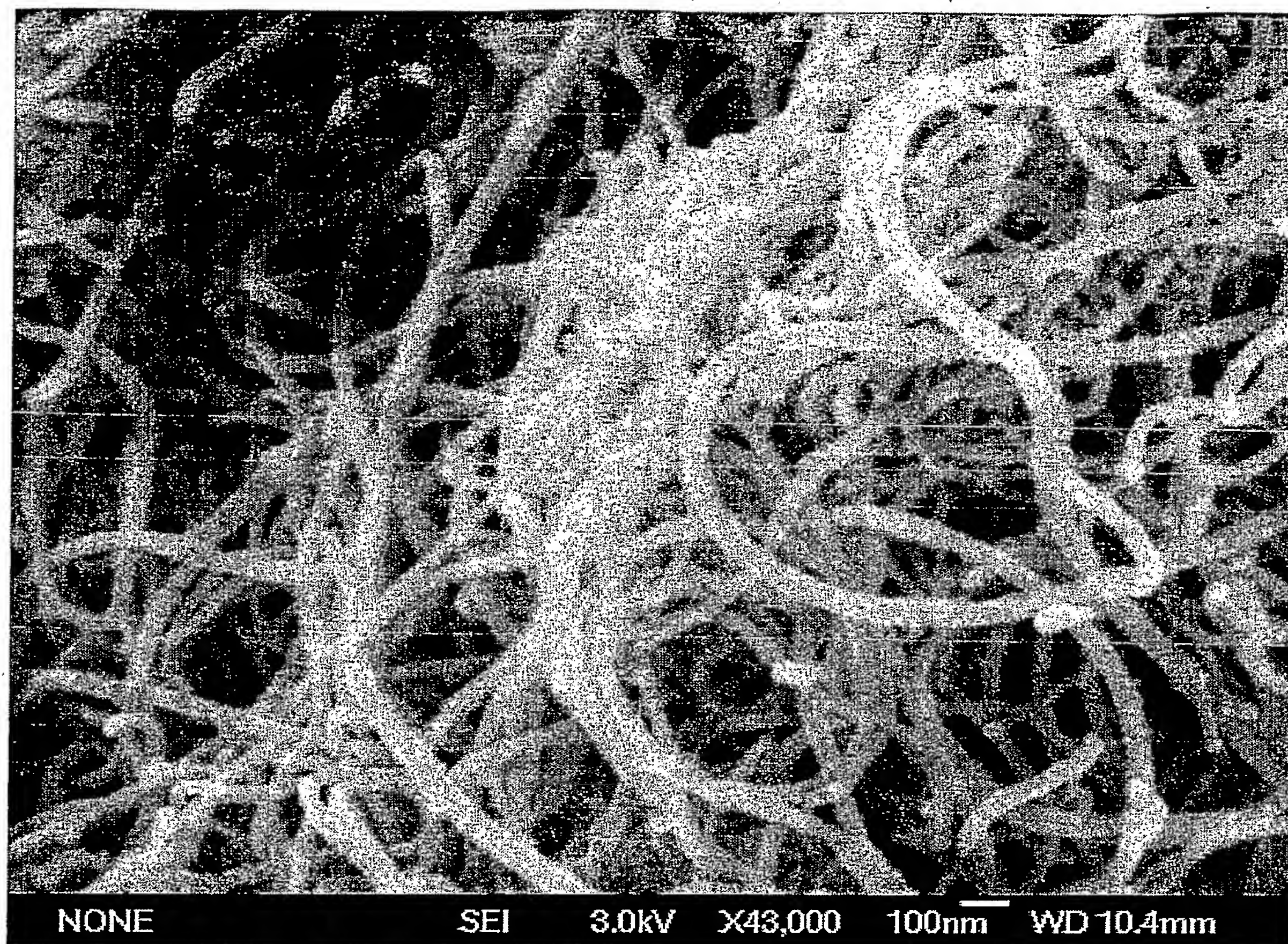


Figure 10b



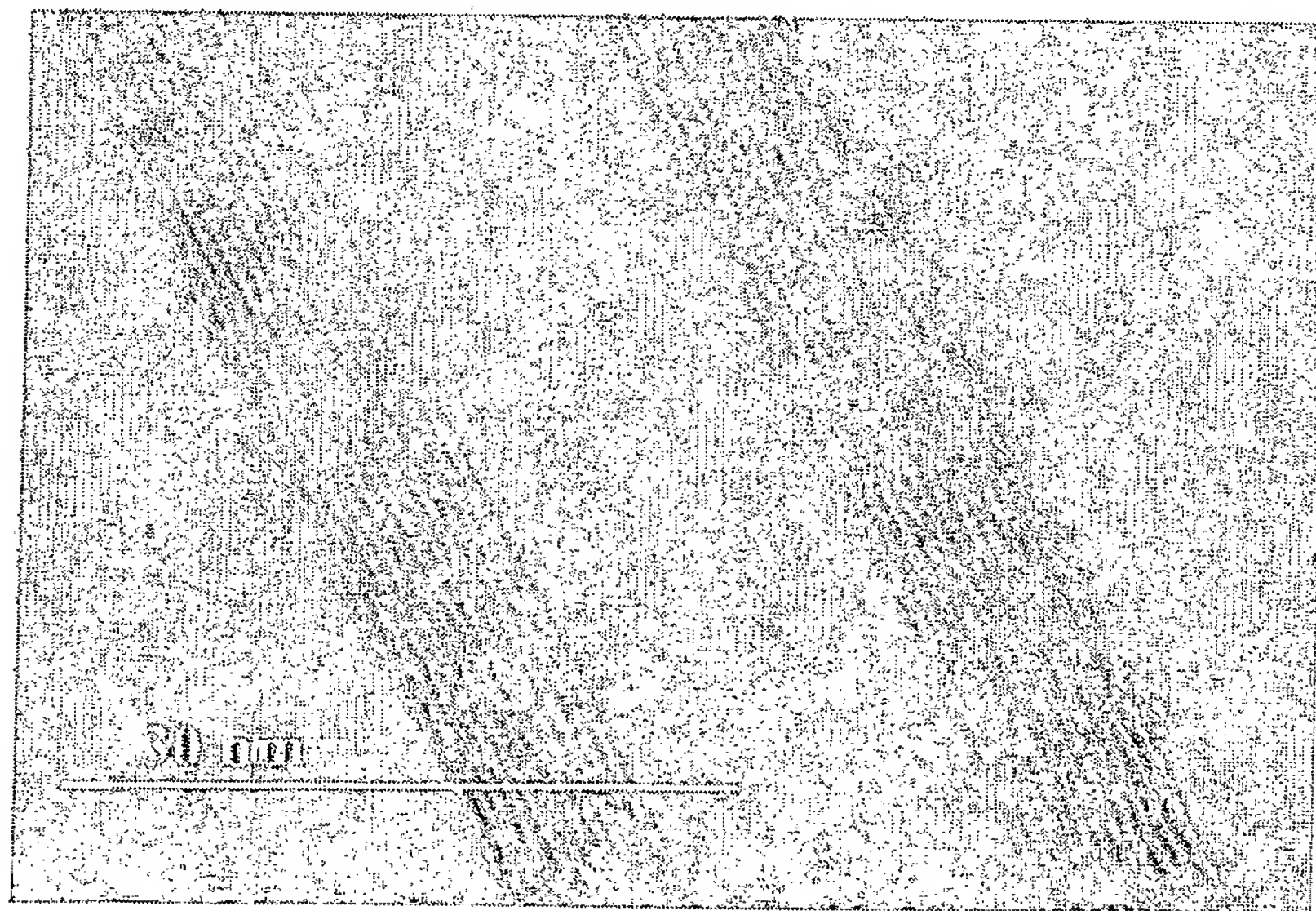
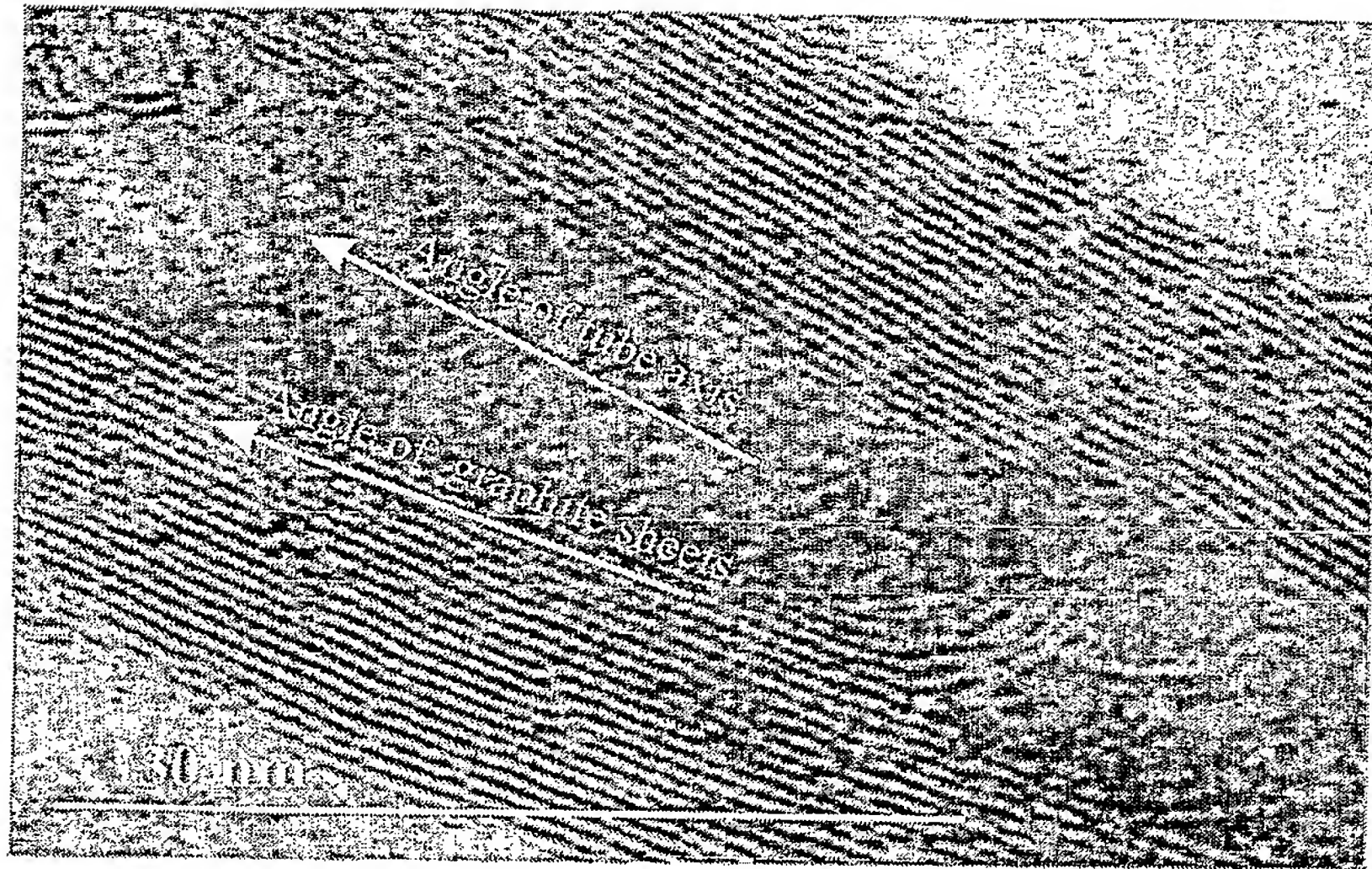


Figure 11a (top) and 11b (bottom)

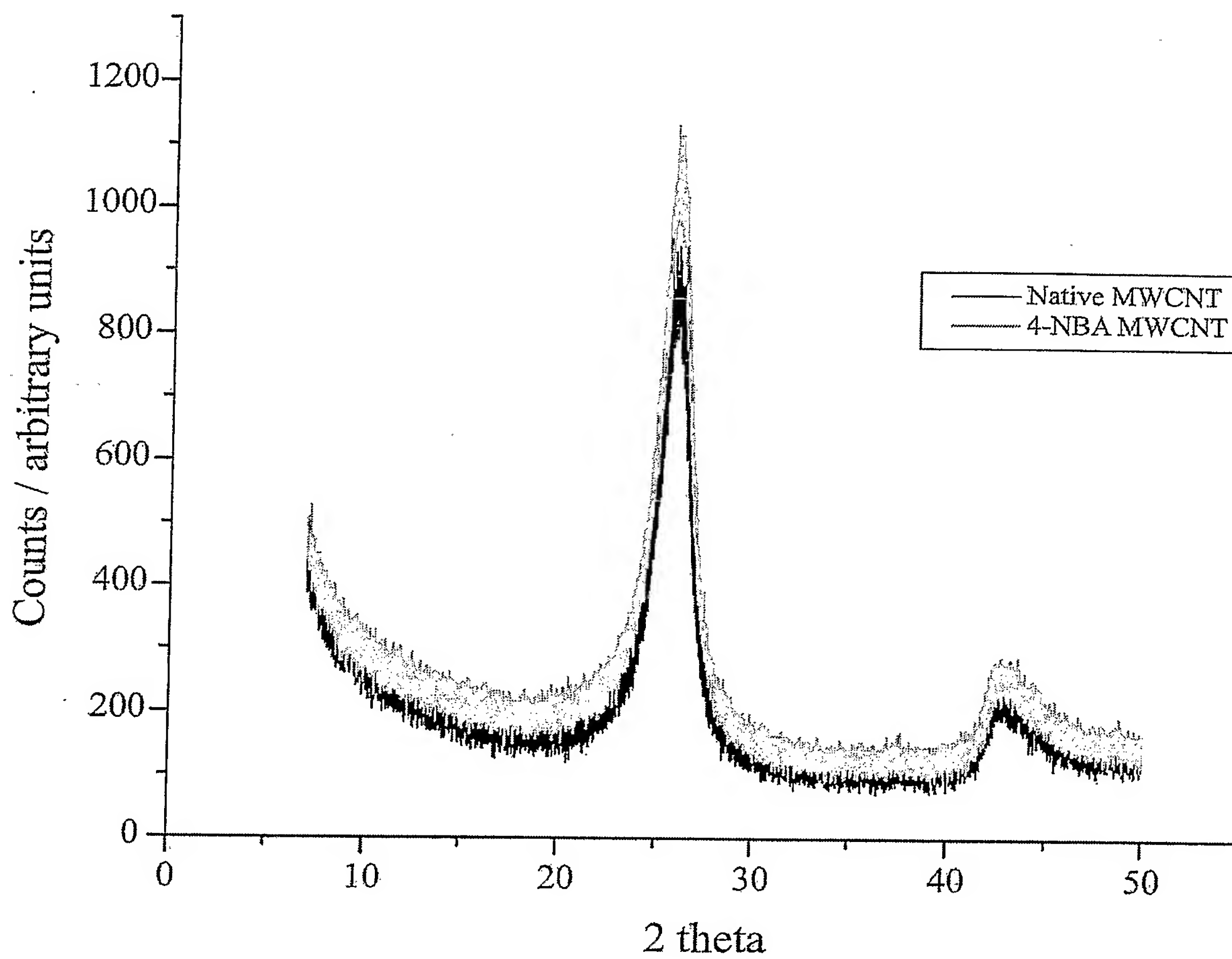


Figure 12

THE PATENT OFFICE

13 APR 2005

Received in Patents
& International Unit